Applications of zinc stable isotope analysis in environmental and biological systems: a review

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Abstract: Zinc (Zn) is an essential trace element that is involved in both biotic and abiotic processes in Earth's surface environments. Over the last 20 years, advances in mass spectrometry instrumentation have enabled unprecedented high-precision Zn isotope abundance ratio determinations in natural and anthropogenic samples. Supported by a solid theoretical background inherited from the traditional non-metal stable isotopes (C, N, H, O, S), the understanding of the controlling factors of Zn isotope fractionation has rapidly evolved. In this article, we review the main applications and findings of Zn isotopes in a variety of scientific domains, including metal contamination, magmatic differentiation, plant uptake, weathering, global climate change, dietary and trophic chains, and biomedicine. The analytical aspects of Zn isotope determination in solid and water samples and the principles and mechanisms of Zn isotope fractionation are also reviewed. This work aims to provide a general yet in-depth panorama of Zn isotope chemistry and to demonstrate the versatility and potential of this isotope system for studying the biological, geological and chemical cycling of Zn.

Keywords: zinc isotopes; isotope geochemistry; trace element mass spectrometry; environmental geochemistry

Over the last 20 years, the analysis of metal stable isotopes has found application in diverse fields, including inorganic chemistry (Veeramani *et al.* 2015), biomedicine (Moynier *et al.* 2013), environmental sciences (Araújo *et al.* 2021; Junqueira *et al.* 2023), anthropology (Jaouen *et al.* 2020), biology (Deng *et al.* 2014; Köbberich and Vance 2019; Araújo *et al.* 2021), climate change (Zhang *et al.* 2022*b*) and mineral exploration geochemistry (Wilkinson *et al.* 2005). A main factor driving this interest is the advance of mass spectrometry and sample preparation methods, now allowing for precise determination of the isotope compositions of metals in a wide variety of natural and anthropogenic materials (Johnson *et al.* 2004; Bullen and Walczyk 2009; Wiederhold 2015; Desaulty *et al.* 2017; Kyser *et al.* 2020).

Zinc (Zn) is among the emerging metal isotope systems of interest to epidemiological, economical, ecological, technological and environmental studies (Caldelas *et al.* 2011; Wiederhold 2015). Zinc is the second most abundant transition metal in organisms (Vašák and Hasler 2000), and a component of ~3000 human proteins. It has many roles in the human body, including contributing to normal growth and development, immunity, cellular homeostasis, cell survival and biochemical functions (Vašák and Hasler 2000; Truong-Tran *et al.* 2001; Andreini *et al.* 2006; Haase and Rink 2014). Zinc also catalyzes reactions and is a cofactor or component of more than 300 metalloenzymes (Rink 2000; Vašák and Hasler 2000). It is thus an essential micronutrient for organisms, but toxic in high concentrations (Cloquet *et al.* 2008). Zinc is used in fertilizers, pesticides and electroplating, and can be released to the environment during mining and metallurgical operations (Sivry *et al.* 2008; Sonke *et al.* 2008; Bigalke *et al.* 2010; Yin *et al.* 2015, 2018). Zinc occurs as a trace element in different geological reservoirs and in biological systems as Zn(II). It is not naturally redox-sensitive in ambient environments but may be reduced to Zn(0) in industrial high-temperature processes or via electrolysis (Wiederhold 2015; Moynier *et al.* 2017). Interpreting the isotopic compositions of primary Zn reservoirs and the mass transfer between these reservoirs can enhance our comprehension of the Zn biogeochemical cycle, whether at a local or global level, and at both microscopic and macroscopic scales (Bullen and Eisenhauer 2009; Rehkämper *et al.* 2012; Albarède 2015; Moynier *et al.* 2017). Recently, reviews of Zn stable isotope systematics have covered specific fields, such as geochemistry (Moynier *et al.* 2017), biomedicine (Schilling *et al.* 2021), botany (Caldelas and Weiss 2017), atmospheric sciences (Schleicher *et al.* 2020) and Zn-contaminated environments (Yin *et al.* 2015), including soils (Wang *et al.* 2021) and aquatic systems (Li *et al.* 2019; Desaulty and Petelet-Giraud 2020). This review incorporates and discusses recent studies on Zn isotopic systematics and emerging applications of Zn fractionation processes across environments, focusing on large-scale patterns of Zn isotope ratios in biogeochemical systems. To this end, Zn isotope biogeochemistry and Zn isotope analysis in fields ranging from metal contamination, magmatic differentiation, weathering, nutrient cycling and palaeoclimate to plant uptake, dietary and trophic transfer, and biomedicine are discussed.

Biogeochemistry of zinc

General chemistry, biological importance and technological applications

Zinc is a chalcophile transition metal that occurs in nature as five stable isotopes, ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn and ^{70}Zn, with isotopic abundances of 49.2, 27.7, 4.0, 18.4 and 0.6%, respectively. It is the 24th most abundant element in Earth's crust, ubiquitous in the environment and with important roles in diverse biotic and abiotic processes in terrestrial and aquatic ecosystems (Frassinetti *et al.* 2006; Cloquet *et al.* 2008; Hambidge *et al.* 2010; Chasapis *et al.* 2012; Maret 2013; Kaur *et al.* 2014). Zinc plays a vital function for living organisms, providing structural integrity to several metabolically important proteins (Frassinetti *et al.* 2006; Rink and Haase 2007; Cloquet *et al.* 2008; Hambidge *et al.* 2010; Chasapis *et al.* 2012; Maret 2013; Kaur *et al.* 2014). In an adult human, about 2 g of Zn are distributed throughout the body, mostly intracellularly in enzymes such as carbonic anhydrase, which interconverts carbon dioxide and bicarbonate and regulates the acid–base balance of the cytosol and superoxide dismutase, which controls reactive oxygen (Tapiero and Tew 2003). Zinc further regulates the glutathione metabolism and metallothionein expression (Cruz *et al.* 2015) and affects signalling pathways and the activity of transcription factors with Zn finger domains (Frassinetti *et al.* 2006; Cloquet *et al.* 2008; Hambidge *et al.* 2010; Chasapis *et al.* 2012; Maret 2013; Kaur *et al.* 2014).

In the Earth's (near-)surface environment, Zn primarily forms chemical bonds with sulfur and oxygen atoms (Albarède 2004). Principal sulfidic Zn ores are sphalerite and wurtzite (ZnS), of the same chemical formula but with distinct crystallographic structures, cubic and hexagonal, respectively. Other important ores are zincite (ZnO), smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4) and hemimorphite [$Zn_4Si_2O_7(OH)_2.H_2O$] (Albarède and Beard 2004). In magmatic silicate rocks, Zn occurs as a trace element (typically 40–120 ppm), whereas it is likely to be concentrated in argillaceous sediments in sedimentary rocks, in the range of 80–120 ppm (Adriano 2001). In coal, Zn concentrations vary from 50 to 19 000 ppm. Mean Zn for worldwide soils is calculated as 64 ppm (Wang *et al.* 2021). The vast majority of Zn produced in the world is derived from sulfidic ores (Cloquet *et al.* 2008). In 2020, the world's Zn reserves were estimated at about 250 million tonnes.

Most of the produced refined Zn (∼60%) is used as a coating to protect iron and steel from corrosion (galvanization), as well as alloying to make bronze, brass and zinc-based die casting (Cloquet *et al.* 2008). Other applications of Zn include as catalysts in the chemical industry (e.g. rubber, pigments, plastic, lubricants and pesticides) and as a component in technological devices such as batteries, screen phosphors and automotive equipment (Meylan and Reck 2017).

In the ocean, Zn displays nutrient-like depth profiles (Mason 2013), reflecting effective scavenging of this element by phytoplankton and posterior regeneration at depth (Conway and John 2014; Zhao *et al.* 2014; Weber *et al.* 2018). The same is observed in pristine lakes and river surface waters (Shiller and Boyle 1985; Lum *et al.* 1991), as well as sediments (Ochieng *et al.* 2008; Xie *et al.* 2019). In terms of groundwater concentrations, studies of these systems have demonstrated the importance of water–rock interactions in controlling the mobility of zinc (Kent *et al.* 2000). However, the extent of these reactions depends on pH and biogeochemical conditions and processes, besides the geological background.

Zinc cycling in the biogeosphere

Zinc is mobilized into the surface environment from natural processes such as weathering and erosion of rocks and soils and volcanic activity. Anthropogenic sources, such as vehicle emissions, sewage sludge, road runoff, industrial emissions and mining and metallurgical wastes, contribute to Zn distribution dynamics as well, and diverse reviews analysing the isotope geochemistry of Zn have been performed in different specific fields (Sparks 2005; Brown and Calas 2011; Little *et al.* 2014; Table 1). Further discussion of the origins and mechanisms of Zn isotope fractionation is provided in Supporting Information S1 and S2.

A variety of Zn compounds are introduced and mobilized into the environment by atmospheric input, groundwater or fluvial fluxes to estuaries and ocean systems, whereas at a geological scale, Zn may be reincorporated as a mineral component through sedimentation (Fig. 1) (Adriano 2001; Sparks 2005). The natural biogeochemical Zn cycle is partially disturbed by anthropogenic remobilization from deep reservoirs to the Earth's surface, most notably from the mining of ores, coal and crude oil, which has led to localized Zn contamination and enrichment of soils, water and air (Wong *et al.* 2006; Mason 2013). At the sediment–water or soil–water interface, Zn can be distributed across particulate (0.45 mm), colloidal (1 nm–0.45 mm) and dissolved metal species (<1 nm) in different chemical forms (Bianchi *et al.* 2007). Its distribution among these different fractions depends on the prevailing physicochemical conditions, including pH, Eh, temperature, ionic strength, as well as suspended particulate and organic matter abundance. This interface is dynamic and many reactions of complexation, adsorption, ion exchange, (co-)precipitation and redissolution of compounds occur concomitantly, with or without biological mediation (Albarède 2008). The combination of these biogeochemical reactions also controls Zn bioaccumulation routes in the trophic chain, e.g. in sediment (benthic organisms) or by uptake of the dissolved fraction in interstitial or surface waters (primary producers including plants,

Table 1. Main reviews on various aspects of Zn isotopes in the environment

| Subject/scope	Year	Reference
Review on Zn isotopes in river systems: distribution and application	2024	Ding *et al.* (2024)
Potential of Zn isotopes in the science and exploration of ore deposits	2023	Wilkinson (2023)
Zinc isotopic signature in tropical soils: a review	2022	Liang *et al.* (2022)
Zinc isotope composition as a tool for tracing sources and fate of metal contaminants in rivers	2020	Desaulty and Petelet-Giraud (2020)
Application of Zn isotope tracer technology in tracing soil heavy metal pollution	2017	Norbu *et al.* (2017)
Isotope geochemistry of Zn and Cu	2017	Moynier *et al.* (2017)
Zinc homeostasis and isotopic fractionation in plants: a review	2017	Caldelas and Weiss (2017)
Application of Zn isotopes in environmental impact assessment of Zn–Pb metallurgical industries: a mini review	2016	Yin *et al.* (2016)
Zinc isotope ratios as indicators of diet and trophic level in Arctic marine mammals	2016	Jaouen *et al.* (2016*a*, *b*)
Zinc isotopes: a novel approach to biomarkers of breast cancer?	2015	Larner *et al.* (2015)
Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: a review	2008	Cloquet *et al.* (2008)
The stable isotope geochemistry of copper and zinc	2004	Albarède (2004)
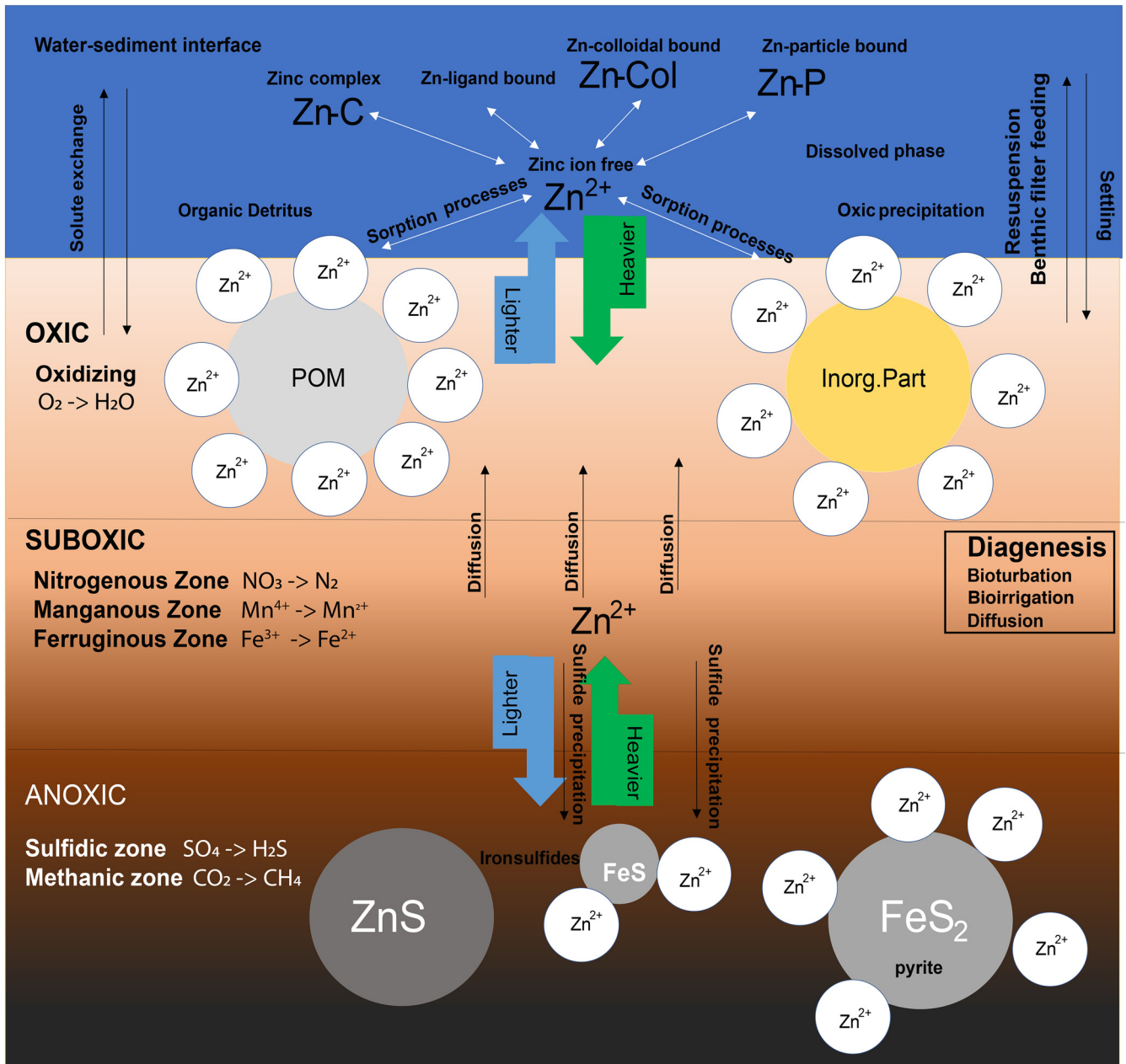
Fig. 1. Aqueous and surface complexes of Zn with different species (ligand, colloid and particle bounds), particulate organic matter (POM) and inorganic particulate (Inorg.Part) in oxic and anoxic environments in the water–sediment interface. The enrichment of lighter/heavier isotopes during diagenesis, diffusion, dissolution and sulfide precipitation are represented by green (heavier isotope) and blue (lighter isotope) arrows.

phytoplankton, macrophytes and bacteria) (Clearwater *et al.* 2002; Zhou *et al.* 2008; Ahlf *et al.* 2009; Andersen *et al.* 2011).

In the solid phase, Zn may exist as an adsorbed species on primary or secondary minerals (clays), oxides, carbonates, sulfides and biogenic compounds generated by biological production or decaying organic matter. In particular, the finest particles and the colloidal fractions of inorganic and biogenic materials play a pivotal role in Zn adsorption due to their significant surface area and surface charge (Turner and Millward 2000; Sparks 2005; Brown and Calas 2011). In the dissolved phase, Zn can exist as a free hydrated ion or form inorganic and organic complexes, including with F^-, Cl^-, SO_4^{2-}, OH^-, HCO_3^-, CO_3^{2-}, HPO_3^{2-}, NH_3 and, in anoxic waters, HS^- and H_2S (Gaillardet *et al.* 2013; Mason 2013). A Pourbaix diagram is provided in Figure S1, showing chemical species as a function of both redox standard potential and pH values. Important organic ligands include humic acids, that may lead to different fractionation proportions depending on the various functional

groups (carboxylic, amino, sulfidic and phenolic) that the free Zn^{2+} has affinity to (Albarède 2008; Jouvin *et al.* 2009).

Sample collection, preparation and analysis

Preventing contamination

Exogenous contamination is a primary concern for Zn isotopic analysis, especially in samples with low Zn concentrations (i.e. samples with <500 ng Zn). Gloves can be an important source of exogenic contamination: in weak acid at room temperature, gloves released up to 17 ng of Zn (Garçon *et al.* 2017). To avoid contamination inside the laboratory, vinyl gloves should be used for biological and geological materials: a single contact between the glove and the labware releases an average of 6 ng of Zn and hence significantly shifts $\delta^{66/64}Zn$ outside measurement uncertainty when the amount of Zn analysed is below 500 ng (Jaouen *et al.* 2020).

Other exogenic contaminant sources may be related to the use of sunscreen, perfume, makeup and other routine chemicals. Zinc is an abundant element, and particularly prone to contamination from care products and sampling equipment. The sampling and protocol performance should be conducted with minimum human contact to prevent contamination. Furthermore, the samples should be stored in plastic containers, and care should be taken to ensure that sampling equipment (e.g. shovels, hammers, augers) does not introduce Zn (Gill 1997). In addition, multiple procedural blanks should be performed in order to monitor the contaminant addition to the sample.

Solid samples

The determination of the Zn isotope composition of solid samples can be performed *in situ* using laser ablation techniques, but the conversion to the dissolved form via acid-dissolution for nebulization and introduction into spectrometers is more common (Becker 2005). For the latter, the bulk sample should be first crushed to facilitate acid dissolution, as well as homogenized (Gill 1997). Sediments and soils normally require freeze-drying (Sivry *et al.* 2008; Araújo *et al.* 2017). Rocks are crushed and ground into fine power using agate, swing or ball mill. In the case of biological tissues, water removal by freeze-drying is crucial to avoid sample deterioration (Gill 1997). After pre-preparation, the samples are dissolved totally on hot plates with mixtures of concentrated acids such as HF, HNO_3 and HCl, preferentially using perfluoralkoxy polymer (PFA) labware (Chapman *et al.* 2006; Araújo *et al.* 2017; Souto-Oliveira *et al.* 2018). In the case of refractory samples, digestion assisted by microwave is often required. Reagents of high purity are desirable to keep blanks as low as possible during the sample preparation; sub-boiling distillation of acids is commonly used (Araújo *et al.* 2017). The sample preparation, as well as dissolution and Zn chromatographic separation should be conducted in an over-pressurized and air-filtered cleanroom equipped with class 100–1000 hoods (Weiss *et al.* 2007; Archer *et al.* 2017; Souto-Oliveira *et al.* 2019).

Aqueous samples

The sampling protocol for Zn isotope analysis of water is similar to that for standard dissolved cation analysis (Chen *et al.* 2009a; Conway *et al.* 2013; Petit *et al.* 2015; Guinoiseau *et al.* 2017). The sample is collected using plastic tubing for pumps or plastic containers for dipping and placed into plastic containers that have been rinsed several times with the water being collected (Chen *et al.* 2009a, b; Conway *et al.* 2013; Petit *et al.* 2015; Guinoiseau *et al.* 2017). Pre-cleaning of the plastic containers with nitric acid is required to assure lower blanks. The water sample needs to be filtered using membranes with a pore size of 0.45 or 0.22 μm (Chen *et al.* 2009a, b; Conway *et al.* 2013; Zhao *et al.* 2014; Petit *et al.* 2015; Guinoiseau *et al.* 2017). Ultra-centrifugation can be used to separate the colloidal phase (e.g. Leybourne *et al.* 2000). After obtaining the dissolved fraction, it should be acidified with nitric or hydrochloric acid to a pH~2 for sample preservation (Chen *et al.* 2009a, b; Conway *et al.* 2013; Zhao *et al.* 2014; Petit *et al.* 2015; Guinoiseau *et al.* 2017). Knowledge of metal concentrations in the sample prior to collection for isotope analysis is essential to ensure that sufficient metal is collected to meet the requirements of the analytical technique. The minimum amount of Zn required for isotope analysis ranges from 100 to 1000 ng, depending on factors such as ionization efficiency in the mass spectrometer, instrumental settings and laboratorial blanks (Maréchal *et al.* 1999; Archer and Vance 2004; Souto-Oliveira *et al.* 2019). After collection, water samples can be dried and additionally digested with acids for posterior analyte separation and analysis (Borrok *et al.* 2007). In

case of very diluted waters or marine waters that contain high dissolved solids, pre-concentration methods can be performed using specific resin packed on columns (such as BioRad Chelex100 and NOBIAS Chelate PA-1) (Chen *et al.* 2008; Conway *et al.* 2013; Takano *et al.* 2017) or through co-precipitation by addition of alkaline compounds to water samples (Bermin *et al.* 2006). As for solid samples as discussed above, chemical procedures of sample preparation, dissolution, pre-concentration and chromatographic separation should be conducted in a cleanroom environment.

Ion exchange separation of Zn: elimination of matrix interferences

To eliminate interferences, Zn must be separated from the sample matrix and particularly from elements that produce isobaric interferences on the target masses for analysis (Becker 2005, Supporting Table S2). Ion-exchange chromatography currently is the preferred technique for this purpose (Maréchal *et al.* 1999; Chapman *et al.* 2006; Sossi et al. 2015; Zhu *et al.* 2015). For Zn, the anionic exchange resin AG MP-1 has been employed in many studies (Maréchal *et al.* 2000; Desaulty *et al.* 2017; Araújo *et al.* 2021). Because the ion-exchange between eluted Zn and resin can fractionate Zn isotopes, a recovery close to 100% is required to avoid significant bias on original isotope compositions of the samples (Jouvin *et al.* 2009). Thus, a prior calibration of chromatography protocols should be performed for the different analysed matrixes to ensure matrix-dependent separation of Zn from other elements. A large number of protocols have been developed, adjusting for specific matrix requirements, or multiple-element separations (e.g. Zn, Cu, Fe, Cd, Mo; Archer and Vance 2004; Luck *et al.* 2005; Mason *et al.* 2005; Schoenberg and von Blanckenburg 2005; Bermin *et al.* 2006; Borrok *et al.* 2007). Generally, these protocols rely on the conversion of Zn (II) free ions to chloride- or bromide-complexes in hydrochloric and bromic acids (Maréchal *et al.* 1999; Moynier *et al.* 2017), and can be performed in the same procedure for other metals such as Cu or Fe (Figure S2).

Analytical challenges

Quantification of isotope ratios

Zinc isotopes can fractionate in mass spectrometers during their transmission from the ICP source to detector (Maréchal *et al.* 1999; Archer and Vance 2004). Therefore, raw Zn isotope composition data should be corrected for induced instrumental fractionation (Maréchal *et al.* 1999; Archer and Vance 2004). One of the techniques used to correct mass bias is the sample standard bracketing (SSB), which consists of analysing an unknown sample 'bracketed' by standards that are used to interpolate and correct mass drift bias during data collection (Archer and Vance 2004; Araújo *et al.* 2017). External normalization, which consists of doping samples and standards with an element with a known isotope composition and similar fractionation behaviour to that of Zn, is another common technique to correct mass bias. Copper-doping is a common choice for Zn isotope analysis (Zhang *et al.* 2022a). The measured isotope ratio of the dopant can be compared to its known value to quantify machine-induced fractionation and the resultant correction is applied to the isotope ratio of the target element (Heumann *et al.* 1998; Archer and Vance 2004; Peel *et al.* 2008; Zhu *et al.* 2015). The double-spike (DS) technique has been applied for Zn isotope determination (Arnold *et al.* 2010), which has advantages over the standard-sample bracketing technique and external normalization as there is no requirement for quantitative yield. However, major difficulties in applying the DS technique are obtaining pure spikes, determining optimal double-spike compositions and double-spike sample mixing proportions, and calibrating

the double spike (Arnold *et al.* 2010; Moeller *et al.* 2012; Costas-Rodríguez *et al.* 2014).

Data reporting and analytical quality control

The Zn stable isotope variations are reported relative to standard reference materials using delta values (δ) expressed as per mil (‰). The $R(^{66}Zn/^{64}Zn)$ ratio is commonly chosen because of the high abundance of these isotopes and is expressed as $\delta^{66/64}Zn$ values as follows:

$$\delta^{66/64}Zn\ (‰) = \left(\frac{R(^{66}Zn/^{64}Zn)_{sample}}{R(^{66}Zn/^{64}Zn)_{standard}} - 1 \right) * 1000. \quad (1)$$

The δ-notation negates the analytical challenge of comparing measured 'absolute' isotope ratios amongst laboratories (Wiederhold 2015). The Zn elemental solution JMC 3-0749 (commonly referred to as the 'JMC-Lyon') and the certified isotope standard IRMM-3702 have been adopted widely (Moynier *et al.* 2017). However, as the first is practically exhausted, the AA-ETH Zn standard (Alfa Aesar Zn foil, Product Code 11912, Lot #I17Z058) and the NIST SRM 683 have been proposed as new primary reference standards for Zn isotope analysis (Archer *et al.* 2017; Yang *et al.* 2018). It is nevertheless recommended to maintain the isotope compositions expressed in relation to the original standard reference materials ('JMC Lyon') to allow a direct comparison with all previously published data, which may be done as follows (Archer *et al.* 2017):

$$\delta^{66/64}Zn_{JMC\text{-}Lyon} = \delta^{66/64}Zn_{AA\text{-}ETH} + 0.28‰. \quad (2)$$

Certified reference materials

Because isotope and elemental standards are synthetic solutions, laboratories commonly analyse certified reference materials such as soils, sediments, plants and rocks to improve quality control (Cloquet *et al.* 2008; Araújo *et al.* 2017; Moynier *et al.* 2017). A compilation of reference materials of geological, environmental, and biological matrixes is presented in Table S1. These reference materials cover much of the variability of $\delta^{66/64}Zn$ in 'natural' Earth surface materials, ranging from −1.00 to 1.00‰. Isotopic compositions of materials with matrix types for more recent applications of Zn isotopes (soil, biological, aqueous) are also provided in Table S1. However, these require further confirmation. Despite numerous studies and applications of Zn isotopes, well-characterized reference materials for more complex environmental samples are noticeably lacking. To unlock additional hydrogeochemical applications of Zn isotopes, reference materials for surface water samples and soil samples are particularly needed.

Controlling factors of Zn isotope variability

Biotic processes

In biotic processes, Zn isotopes are fractionated when they are transferred between different enzymes to which Zn is bound. This concept has been elucidated in studies conducted by Moynier *et al.* (2013) and Fujii *et al.* (2014). Zinc distribution, as well as its fractionation, within living organisms is partially controlled by the supplied concentration and by the type of cellular Zn transporters (Caldelas *et al.* 2011; Deng *et al.* 2014; Weiss *et al.* 2021).

Studies on Zn isotope fractionation have been performed to elucidate the mechanisms of Zn transport in soils and plants (Weiss *et al.* 2005; Bigalke *et al.* 2010), metabolism changes (Albarède *et al.* 2017), biological productivity (Andersen *et al.* 2011) or fractionation during uptake by microorganisms (Balistrieri *et al.* 2008; Jouvin *et al.* 2009).

In plants, there is a notable fractionation of Zn during transport from the roots to the shoots and its transfer from vegetative to reproductive tissues (Caldelas *et al.* 2011; Arnold and Wade 2015; Wiggenhauser *et al.* 2018). Heavy Zn tends to form chelates, and in the shoot, it is retained through apoplastic absorption (Caldelas *et al.* 2011; Aucour *et al.* 2017; Wiggenhauser *et al.* 2018): Zn isotopic fractionation in soil–plant systems can vary depending on the availability of Zn, which in turn is influenced by soil properties (Fig. 2). Therefore, the Zn isotope compositions can serve as a valuable tool for detecting changes in biogeochemical processes that govern the distribution of zinc in soil–plant systems in response to alterations in soil environments.

Whereas many studies are related to Zn fractionation during plant uptake, Zn isotopic fractionation during internal plant processes and transport remain more enigmatic (Caldelas and Weiss 2017; Wiggenhauser *et al.* 2018). Wiggenhauser *et al.* (2018) studied Zn isotope ratios in wheat shoots at different growth stages in order to understand the main pathways and processes during grain filling, and concluded that Zn mass is inversely proportional to the heavy isotope accumulation: 75% of the total Zn mass in the shoot moved to the grains, which are enriched in light isotopes relative to the straw ($\delta^{66/64}Zn$ grain–straw = −0.31 to −0.21‰). This corroborates previous studies showing that light Zn isotopes are accumulated in phloem sinks and heavy isotopes are retained in phloem sources.

Numerous investigations over the past few decades have focused on Zn fractionation in diatoms (e.g. Gélabert *et al.* 2006; John *et al.* 2007) and bacteria (e.g. Wanty *et al.* 2013). Additionally, Peel *et al.* (2009) and Andersen *et al.* (2011) have demonstrated that Zn isotopes found in particulate matter and diatom frustules can be used as indicators for tracing the biochemical cycling of Zn. Despite this attention, the relative importance of surface complexation v. intracellular incorporation on Zn isotope fractionation remains debated. For instance, Gélabert *et al.* (2006) demonstrated that in sorption and uptake processes, both freshwater and seawater diatoms exhibited a preference for heavier Zn, with $\Delta^{66/64}Zn$ cell-solution values of 0.35 and 0.27‰, respectively. In contrast, an experimental study by John *et al.* (2007) reported that low Zn concentrations in media drove high-affinity uptake and a more negative isotope fractionation effect ($\Delta^{66/64}Zn_{cells\text{-}medium} = -0.8‰$) compared to low affinity transport when more Zn is available ($\Delta^{66/64}Zn_{cells\text{-}medium} = -0.2‰$) (John *et al.* 2007). Furthermore, Kafantaris and Borrok (2014) conducted experiments under a variety of conditions (e.g. pH, time or growth phase), and concluded that bacterial adsorption preferentially incorporates the heavier isotope, but the extension of the uptake, and then fractionation, is strongly related to the presence of dissolved organic molecules and free Zn^{2+} in the environment of growth.

There remains uncertainty regarding the extent of Zn isotopic fractionation among different bacterial species and under varying conditions of Zn stress. Furthermore, there is a lack of knowledge regarding the roles of cell surface adsorption and speciation of aqueous Zn on the extent of isotopic fractionation. Although Zn isotopes hold promise as tools to elucidate the metal-binding pathways linked to microorganisms in natural environments, the interpretation of the isotopic compositions is complicated by the presence of competing surface interactions, metal speciation, and differing impacts of various microbial species.

Zn isotope fractionation in cosmochemistry

Investigations of the Zn isotope composition of meteorites showed $\delta^{66/64}Zn$ values spread over a range of +0.3‰ for carbonaceous chondrites and 2‰ for ordinary chondrites (Bridgestock *et al.* 2014; Moynier *et al.* 2017). All meteoritic and terrestrial samples plot on the same mass-dependent fractionation line, implying that Zn from the inner solar system formed from a single isotopically homogeneous reservoir (Luck *et al.* 2005). For CI chondrites, $\delta^{66/64}Zn$ values of +0.46 ±
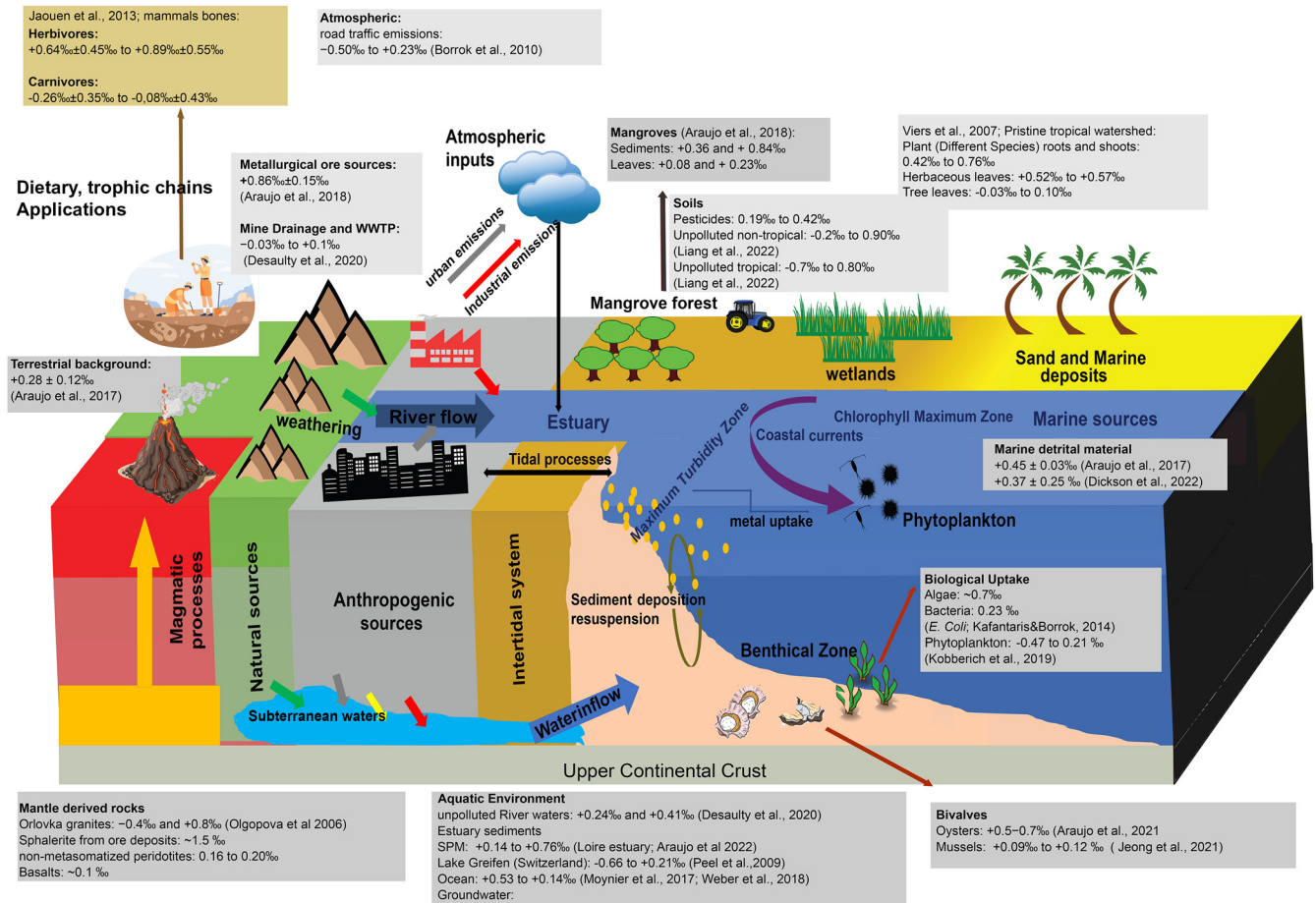
Fig. 2. $\delta^{66/64}$Zn applied to mantle-derived rocks, aquatic environments, pristine tropical watersheds, mangroves, soils, atmospheric input, marine detrital material, metallurgical ore sources, mine drainage and wastewater treatment plant (WWTP), dietary and trophic chain, biological processes and biomedicine. SPM, suspended particulate matter.

0.08‰ have been used as a best estimate for the primordial Zn isotope composition of the Solar system (Moynier *et al.* 2017). The large range of Zn isotope compositions observed in the most part of primitive meteorites seems related to the variable mixing of isotopically distinct components in the case of the carbonaceous chondrites (Luck *et al.* 2005), and in the case of the ordinary and EL enstatite chondrites, related to thermal reworking on parent bodies (Moynier *et al.* 2017). In turn, ureilite samples showed a range of $\delta^{66/64}$Zn values ~0.7‰ and a negative correlation between the abundance of Zn and $\delta^{66/64}$Zn values, which suggests isotope fractionation occurred by evaporation during the heating event on the ureilite parent body generated by possible impacts (Moynier *et al.* 2010).

Zinc isotope variation in silicate rocks (including igneous, metamorphic and sedimentary) is small and tends to cluster within a narrow range of +0.20 to +0.40‰ (Chapman *et al.* 2006; Cloquet *et al.* 2008; Herzog *et al.* 2009; Moynier *et al.* 2009a; Chen *et al.* 2013). Investigations on suites of volcanic rocks have shown that high-temperature igneous processes induce fractionations no larger than 0.10‰, and therefore Zn isotopes seem limited in revealing planetary formation and differentiation processes. Based on those findings and assuming a homogeneous Earth's mantle and that Zn is not partitioned into the core, the Zn isotope composition for the bulk Earth is estimated at +0.28 ± 0.05‰ (2σ) (Chen *et al.* 2013). The overall homogeneous Zn isotope composition of the Earth is most likely the result of large-scale melting, mixing and differentiation events that occurred in the terrestrial mantle during and post-accretion (Chen *et al.* 2013). Despite this apparent global homogeneity, some geological settings with contrasting $\delta^{66/64}$Zn values have been reported in the Taiwan orogeny and in granites from the Lachlan Fold Belt (Australia) (Telus *et al.* 2012).

Continental basalts in eastern China showed a large range of $\delta^{66/64}$Zn values, from +0.30 to +0.63‰, a possible result of the recycling of isotopically heavy marine carbonates ($\delta^{66/64}$Zn average of +0.91‰) during marine plate subduction processes (Liu *et al.* 2016).

Because Zn is a moderately volatile element (condensation at ~730 K), Zn isotope signatures have the potential to reveal evaporation–condensation processes in actively degassing volcanoes, planetary bodies such as lunar samples, and shocked rocks from terrestrial impact craters such as tektites. At Merapi Volcano degassing, the gas cooling from 590 to 297°C is accompanied by a decrease in Zn concentrations of the gaseous phase, which becomes gradually enriched in the light Zn isotope, while the condensates become progressively enriched in the heavier isotopes (Toutain *et al.* 2008). Gas and condensate isotope compositions could be explained by a Rayleigh condensation mode (Toutain *et al.* 2008). The $\delta^{66/64}$Zn of lunar basalt is ~1‰ heavier than terrestrial basalt, suggesting that this fractionation occurred during a large-scale evaporation event, likely related to the giant impact that originated the Moon (Paniello *et al.* 2012). Tektite samples also showed broader $\delta^{66/64}$Zn values than the terrestrial crust, encompassing lighter values of +0.3‰ to anomalous values of +2.49‰ (Moynier *et al.* 2009a). All these were negatively correlated with Zn abundance, implying that isotope fractionation occurred by evaporation during the heating event upon tektite formation (Moynier *et al.* 2017).

Terrestrial rocks and volcanic systems

Understanding the controls on Zn isotopic variability in rocks and minerals can provide insights into the geological processes

that have influenced the formation and evolution of Earth materials. The potential of the Zn isotope system as a tracer of geological processes happening on Earth has been extensively studied in the past decade (Johnson *et al.* 2004; Cloquet *et al.* 2008; Moynier *et al.* 2017; Mathur *et al.* 2021; Wilkinson 2023) due to the significantly fractionation during continental weathering, carbonate and sulfide precipitation, and fluid–rock interactions.

Within Earth's interior, at high temperature and pressure, there are four possible mechanisms that can lead to heavy Zn isotopic compositions in basalts, including: (1) crystal-melt differentiation, which occurs when there is crystallization of olivine and/or Fe–Ti oxides at the very end of the differentiation sequence (Chen *et al.* 2013; Sossi et al. 2015); (2) magmatic degassing, which shows significant Zn isotope fractionation, with gas condensates enriched in the heavy isotopes (Chen *et al.* 2013); (3) crustal contamination, for example with sedimentary carbonates while it ascends through the crust (Liu *et al.* 2016); and/or (4) isotopic heterogeneity caused by recycled materials in the mantle sources, via plate subduction (Zhao *et al.* 2014; Liu *et al.* 2016). Zinc isotopes can be used to constrain the evolution of the Earth and processes involved, besides being useful as a proxy for planetary differenti-ation and volatile history (Chen *et al.* 2013; Liu *et al.* 2016; Wang *et al.* 2021).

Zinc isotope variation in silicate rocks (including igneous, metamorphic and sedimentary) is small and values tend to cluster within a narrow range of 0.20–0.40‰ (Chapman *et al.* 2006; Cloquet *et al.* 2008; Herzog *et al.* 2009; Moynier *et al.* 2009*a, b*; Chen *et al.* 2013). Investigations on suites of volcanic rocks have shown that high-temperature igneous processes induce fractiona-tions no larger than 0.10‰ and, therefore, Zn isotopes may not be very useful to assess geological differentiation processes. The overall homogeneous Zn isotope composition of the Earth is most likely the result of large-scale melting, mixing and differentiation events that occurred in the mantle during and post-accretion (Chen *et al.* 2013). In spite of this apparent global homogeneity, some cases of geological settings with contrasting $\delta^{66/64}$Zn values have been reported in the Taiwan orogeny and in granites from Lachlan Fold Belt (Australia) (Telus *et al.* 2012). In some cases, the isotopic composition of Zn in rocks may be influenced by the mixing of different Zn sources with different isotopic compositions. For example, the mixing of isotopically distinct Zn sources during magma genesis can result in isotopic variation in volcanic rocks (Chen *et al.* 2013).

The $\delta^{66/64}$Zn values of clay minerals from sedimentary rocks (e.g. shales, sapropels, aeolian dust, and Pacific and Atlantic sediments) display a range of 0.17–0.35‰ (Maréchal *et al.* 2000; Albarède 2004) and show little variability with respect to their precursor rocks. Besides the extensive studies on Zn isotopes in sedimentary rocks, the relationship of bulk carbonate $\delta^{66/64}$Zn to seawater is poorly understood (Müsing *et al.* 2022). Whereas inorganic carbonate records heavier $\delta^{66/64}$Zn values compared with the aqueous phase (e.g. incorporation into and adsorption on to inorganic calcite; Mavromatis *et al.* 2019), biogenic carbonates from modern cold-water corals and foraminifera record the ambient seawater $\delta^{66/64}$Zn, and indicate negligible fractionation (Little *et al.* 2014). Consequently, there appear to be different fractionation patterns for Zn in carbonates, depending on the precipitation pathway (Müsing *et al.* 2022). The potential of contamination from different phases (i.e. ferromanganese-oxide coatings, as well as detrital silicate and organic matter), as well as the relationship between $\delta^{66/64}$Zn from modern seawater and those incorporated into carbonate, is poorly understood (Müsing *et al.* 2022). Therefore, for palaeoceanography applications, the pathways of carbonate pre-cipitation and associated Zn fractionation processes should be further explored.

Soils

Soils show a large range of Zn isotope compositions in relation to parental rock (0.18–0.55‰ in unpolluted soils; Fekiacova *et al.* 2015; Fig. 2), which is attributed to the combination of natural abiotic and biological processes involved in the redistribution of Zn into different soil horizons during pedogenesis (Viers *et al.* 2007). Literature compilations demonstrate a general tendency of $\delta^{66/64}$Zn values centred on 0.1‰ and on 0.2‰ in the B and O horizons, respectively (Fekiacova *et al.* 2015), but establishing general principles of Zn isotope fractionation in soils is challenging due to the combined roles of aqueous chemistry, weathering, mineralogy, amorphous solids and organic matter in Zn isotope fractionation within different soil horizons (Vance *et al.* 2016; Moynier *et al.* 2017). Soils with a low degree of weathering from Central Siberia presented almost constant $^{66}\delta$Zn values (~0.2‰) close to basalt parental rocks (Viers *et al.* 2015). Zinc isotope data for soil profiles from Hawaii and Scotland, covering both granitoid and basaltic substrates, showed little isotope variations (<0.2‰), and are associated with material removal by weathering, effects of redox transitions on sorption substrates and reactions with organic ligands (Vance *et al.* 2016). The partitioning of Zn isotopes between aqueous organic complexes and particulate oxyhydroxide surfaces is likely the key factor for Zn isotope fractionation in soils (Vance *et al.* 2016).

Furthermore, the Zn isotope geochemistry of soils is affected by biological activity, which has an important role in recycling metals through the biogeosphere (Caldelas and Weiss 2017). Previous studies have demonstrated significant Zn isotope fractionation on the continuum soil–plant (Viers *et al.* 2007) and large isotope variations during uptake, translocation and distribution of Zn between the internal compartments of plants (Moynier *et al.* 2009*b*; Weinstein *et al.* 2011; Jouvin *et al.* 2012; Couder *et al.* 2015; Caldelas and Weiss 2017; Martín *et al.* 2018). The magnitude and direction of fractionation are related to the interspecies character-istics, nutrient uptake strategies and solution concentrations, elemental speciation, ligands, transpiration flow and height, amongst others (Moynier *et al.* 2009*b*; Weinstein *et al.* 2011; Jouvin *et al.* 2012; Couder *et al.* 2015; Caldelas and Weiss 2017; Martín *et al.* 2018). Models of the Zn transference across the root cell membrane have been based on kinetic fractionation with preferential incorporation of the light isotope via diffusion in low-affinity plants; or with preferential heavy isotope incorporation via Zn complexation in carrier-mediated transport (e.g. zinc/iron-regulated protein, ZIP) in high-affinity pathways (Jouvin *et al.* 2012). The preferential adsorption of the heavy isotope on the cell wall of roots may also be responsible for lighter Zn isotope composition in solution. The pattern of Zn isotope compositions in plants may also vary depending on the toxic conditions of the grown medium, where preferential uptake of the heavy isotope of Zn in the roots results in the absorption of the light isotope in the aerial compartments (Couder *et al.* 2015). In mangroves close to Rio de Janeiro (Sepetiba Bay), leaves of *Laguncularia racemose* showed different $\delta^{66/64}$Zn values between highly Zn-contaminated (0.08‰) and low Zn (0.23‰) mangroves (Araújo *et al.* 2018).

Finally, the soil mineralogy can have a significant impact on the isotopic composition of Zn. Different minerals may have different isotopic signatures, and the weathering of minerals can lead to fractionation of Zn isotopes (Liu *et al.* 2020). Soil pH can affect the availability and mobility of Zn in soils, which can in turn influence the isotopic composition of Zn. For example, in acidic soils, Zn may be more mobile and may undergo more isotopic fractionation than in alkaline soils (Wisawapipat *et al.* 2017). The presence of organic matter in soils can also affect the isotopic composition of Zn. Organic matter can influence the adsorption and desorption of Zn, which can affect its isotopic composition (Gu *et al.* 2022). Microbial activity in soils can also affect the isotopic composition

of Zn: microbes can alter the speciation and availability of Zn in soils, leading to isotopic fractionation (Liu *et al.* 2023).

Aqueous environment

A variety of processes control metal fractionation in the aqueous environment, including equilibrium isotope distribution between dissolved aqueous species and equilibrium/kinetic effects due to processes as adsorption, precipitation, dissolution, and uptake from live organisms (Desaulty *et al.* 2017). The main physical and chemical processes governing the isotope compositions of Zn in the aqueous environment are: Zn uptake by microorganisms and plants, adsorption on to mineral particles and biological surfaces; complexation with organic matter, mineral phase precipitation and dissolution (Fig. 2) (Pokrovsky *et al.* 2005; Weiss *et al.* 2005; Viers *et al.* 2007; Balistrieri *et al.* 2008; Fernandez and Borrok 2009; Jouvin *et al.* 2009, 2012; Caldelas *et al.* 2011; Veeramani *et al.* 2015; Guinoiseau *et al.* 2016).

Although there are various studies on Zn isotope systematics in rivers, many of these are in or near contaminated sites and consequently show isotopic variations between natural and anthropogenic Zn (Araújo *et al.* 2019; Ding *et al.* 2024). For Zn geogenic sources, similarities between siliciclastic rocks and marine detrital sediments are observed, hindering the interpretation of the distinguished geological sources (Cloquet *et al.* 2008; Petit *et al.* 2015). In rivers that are unaffected by anthropogenic activities, Zn concentrations (in solution) are generally between 1 and 2 µg l^{-1} (Gaillardet *et al.* 2013; Desaulty *et al.* 2017), and the $\delta^{66/64}$Zn composition can vary between 0.23 and 0.55‰ (Ding *et al.* 2024). However, $\delta^{66/64}$Zn values can show greater variability resulting from natural processes in the aqueous environment. An example in an estuary in France showed progressive enrichment in light isotopes due to mixing (Araújo *et al.* 2017), which were similar in range to the temporal variations of $\delta^{66/64}$Zn values in particulate matter from a temperate Swiss lake (Lake Greifen) (Peel *et al.* 2009). These samples showed distinct variations from −0.66 to 0.21‰ with the highest negative values observed in the summer, during the period of high primary productivity, and most positive values from May to July. The observed temporal pattern is consistent with the preferential uptake of the lighter Zn isotopes during photosynthesis and incorporation of Zn into the algal material (John *et al.* 2007), which results in the depletion of Zn in the surface waters and at the same time the enrichment of the heavier Zn isotopes in the residual dissolved and particulate Zn pool. At the end of the productive period, the algal detrital material enriched in the light isotope contribute to bulk particulate matter, leading the particulate Zn pool to lighter isotope compositions. Although Zn isotopes can be successfully applied to aqueous analysis, these measurements can be challenging due to the low Zn concentration in most pristine environments, resulting in difficult purification processes during Zn chromatography.

Fluvial and marine sediments

In oligotrophic systems, both fluvial and terrestrial sediments seem to inherit the lithogenic Zn isotope composition (Little *et al.* 2014; Fig. 2). In turn, the Zn dissolved pool of rivers and estuaries shows a large range of $\delta^{66/64}$Zn values associated with the multitude of biogeochemical processes involved in Zn transport in waters (Petit *et al.* 2015; Szynkiewicz and Borrok 2016). Amongst them and of pivotal importance are adsorption processes. Various works have investigated, using controlled experimentation, the isotope effects related to aqueous–solid interactions in variable pH values and ionic strength conditions. Overall, the adsorption of Zn on solid surfaces (such as mineral particles and membranes) generally lowers the $\delta^{66/64}$Zn of dissolved Zn in solution because of the preferential incorporation of heavier Zn isotopes during adsorption (Pokrovsky *et al.* 2005; Balistrieri *et al.* 2008; Juillot *et al.* 2008; Dekov *et al.* 2014; Kafantaris and Borrok 2014; Dong and Wasylenki 2016; Guinoiseau *et al.* 2016). At the surface of kaolinite, the fractionation between the adsorbed pool and the solution ($\Delta^{66/64}$Zn$_{adsorbed-solution}$) ranged from 0.11‰ at low pH and low ionic strength to 0.49‰ at high pH and high ionic strength (Guinoiseau *et al.* 2016). The Zn isotope fractionation at the surface of Fe-oxides with respect to the coexisting solution is reported, with $\Delta^{66/64}$Zn$_{solid-solution}$ of 0.29 ± 0.07‰ and 0.53 ± 0.07‰ (ferrihydrite; Balistrieri *et al.* 2008; Juillot *et al.* 2008). For Zn adsorption on birnessite (MnO$_2$·nH$_2$O), Zn isotopes showed limited fractionation at low ionic strength, while heavy Zn isotopes are sorbed preferentially at high ionic strength ($\Delta^{66/64}$Zn$_{solid-solution}$ from 0.52 to 0.77‰) (Bryan *et al.* 2015). Regarding the organic matter, Zn binds to the phenolic sites of purified humic acid with a $\Delta^{66/64}$Zn$_{solid-solution}$ = 0.24 ± 0.06‰ (Jouvin *et al.* 2009).

In agreement with the laboratory results, a field study on Rio Grande (USA) performed by Szynkiewicz and Borrok (2016) reported that an increase in fluid pH from 7.5 to 8.5 led to a considerable decrease in the $\delta^{66/64}$Zn of dissolved Zn and to isotope fractionation between the adsorbed and dissolved pool ($\Delta^{66/64}$Zn$_{adsorbed-dissolved}$) of 0.31‰. However, in contrast, in the Gironde estuary (France), the dissolved Zn showed an enrichment in heavy isotopes relative to the fluid due to the preferential sorption of the light Zn isotope on to suspended particulate matter (Petit *et al.* 2015; Zimmermann *et al.* 2020). The sorption of the lighter isotope may be associated with kinetically driven adsorption caused by the strongly increasing of sorption sites (i.e. removal on to suspended particulate matter) in the water mixing zone of the estuary. The same is observed in the mixing zone of the Solimões River and Negro River (Amazonia, Brazil), where Zn isotope composition of the dissolved pool is fractionated during adsorption on to the suspended sediments and suspended particulate matter (Guinoiseau *et al.* 2018). Other laboratory experiments have shown significant Zn isotope fractionation during chemical diffusion, mineral precipitation, and biological incorporation by the phytoplankton. Veeramani *et al.* (2015) showed an increasing trend to heavier values of $\delta^{66/64}$Zn in solution during sphalerite (ZnS) formation but decreasing trend in $\delta^{66/64}$Zn during the precipitation of hydrozincite (Zn$_5$(CO$_3$)$_2$(OH)$_6$) and hopeite (Zn$_3$(PO$_4$)$_2$·4H$_2$O).

Data from the Southern Ocean, North Atlantic and North Pacific Ocean are strikingly homogeneous, with an average $\delta^{66/64}$Zn = 0.53 ± 0.14‰ (Conway and John 2014; Little *et al.* 2014; Zhao *et al.* 2014; Moynier *et al.* 2017; Weber *et al.* 2018). In contrast, the upper ocean exhibits more variability, with $\delta^{66/64}$Zn ranging from 0.07 to +0.80‰ (Zhao *et al.* 2014). A thin horizon at 40–80 m with lighter $\delta^{66/64}$Zn values close to 0.30‰ has been attributed to the preferential biological uptake of the light isotope (Little *et al.* 2014; Zhao *et al.* 2014; Moynier *et al.* 2017). Primary productivity and the preferential removal of the light isotope could explain the heavier isotope compositions of authigenic marine sediment, including Fe–Mn nodules ($\delta^{66/64}$Zn = 0.90 ± 0.28‰; Fig. 2; Maréchal *et al.* 2000), biogenic carbonates ($\delta^{66/64}$Zn = 0.91 ± 0.24‰; Pichat *et al.* 2003) and biogenic opal ($\delta^{66/64}$Zn = 0.76– 1.47‰; Andersen *et al.* 2011). However, estimates on mass balance between inputs and outputs of Zn isotopes on the oceans do not match, implying that a missing light sink is still to be located (Little *et al.* 2014). Although the number of seawater samples presented in papers related to Zn isotopes has increased in the past decade (14 in 2010, 2000 in 2020; Conway *et al.* 2021), there remains a need for studies on the processes influencing Zn fractionation in high-latitude regions, as these regions present a key knowledge gap for understanding the global biogeochemical Zn cycle (Conway *et al.* 2020). Other studies on $\delta^{66/64}$Zn in aquatic

environments have revealed the importance of ferromanganese crusts as potential palaeoceanographic archives of Cu and Zn. For instance, He *et al.* (2023) show that, in contrast to Cu, the $\delta^{66/64}$Zn values of Fe–Mn crusts are isotopically heavy when compared with deep seawater (0.94 ± 0.21‰ v. 0.51 ± 0.14‰) (Fig. 1).

Applications of zinc isotopes in acid mine drainage

In various studies of Zn in acid mine drainage (AMD), the Zn isotope signatures of the dissolved phase have appeared similar to the original ores (sphalerites, for example) and often correlated with geochemical parameters (pH, ionic strength and temperature) (Borrok *et al.* 2008; Fernandez and Borrok 2009). This conservative behaviour indicates that Zn isotopes are more likely to be tracers of sources rather than attenuation processes in the AMD context (Skierszkan *et al.* 2016). However, studies conducted in an alkaline-pH river (pH~8) with an elevated dissolved Zn load from mining activities showed that some Zn is removed during precipitation of Zn-carbonates and amorphous Zn-silicate minerals, which had $\delta^{66/64}$Zn values heavier than the dissolved Zn pool (Wanty *et al.* 2013). Further controlled laboratorial experiments confirmed that carbonate precipitation removes heavy Zn isotopes from solution (Veeramani *et al.* 2015).

Zn isotopes applied to geochemical exploration

Zinc isotopes fractionate during igneous processes, fluid exsolution, mineral precipitation and supergene processes. Thus, different types of Zn deposits have different Zn isotopic characteristics and variability: Zn isotopes have the potential to trace metal source and provide information into ore-forming processes (Fig. 2). Zinc isotope studies have been conducted in ore deposits, such as on the Alexandrinka volcanic-hosted massive sulfide deposit (VHMS) (Mason *et al.* 2005), the carbonate-hosted Zn–Pb deposits of the Irish Midlands ore field (Wilkinson *et al.* 2005), the Red Dog shale-hosted base metal deposit (SEDEX) (Kelley *et al.* 2009), and modern submarine hydrothermal systems (John *et al.* 2008). The above have shown that the Zn isotope composition of sphalerite is controlled by the composition of the source-rock(s), and temperature-related and kinetic fractionation during precipitation of sulfides (Pašava *et al.* 2014). Based on a compilation of datasets published in the literature for Zn ores sulfides, Sonke *et al.* (2008) calculated an average of $\delta^{66/64}$Zn of 0.16 ± 0.20‰ (2s, $n = 10$ mines, $n = 61$ analyses). Zinc isotope fractionation in secondary Zn minerals formed during low-temperature hydrothermal and/or supergene oxidation of primary sulfide deposits collected from several Zn deposits in Ireland, Belgium, Poland, Namibia, Peru, Yemen and Zambia presented values ranging from -0.42 to 1.39‰ (Mondillo *et al.* 2018). Coal and fuel mixtures present $\delta^{66/64}$Zn values from 0.13 to 0.88‰ (Borrok *et al.* 2010; Ochoa Gonzalez and Weiss 2015). This range is suggested to be related to different Zn speciation and diagenetic processes in the precursor material of the coal (Ochoa Gonzalez and Weiss 2015).

In a review by Mathur and Wang (2019), the application of Zn isotopes in geochemical exploration is explored in different deposit types, including VHMS, SEDEX and carbonate hosted Zn-deposits. For instance, for the VHMS deposits, a Rayleigh distillation model is proposed by several authors to explain the increasing trend in $\delta^{66/64}$Zn (Maréchal *et al.* 2000; Archer and Vance 2004; Borrok *et al.* 2008; John *et al.* 2008), suggesting that sulfides are enriched in ^{64}Zn during early phase diagenesis, which cause the heavier $\delta^{66/64}$Zn values in the residual fluids. There is a gradual increase of this signature from early to late stages in this type of deposit (i.e. from the sphalerite core to rim; Mason *et al.* 2005; Mathur and Wang 2019).

Emerging applications

Climate change

According to Mahowald *et al.* (2006), mineral dust aerosols have the potential to affect the global climate by influencing the radiative balance of the atmosphere and the supply of micronutrients to the ocean. From this premise, Zhang *et al.* (2022b) applied Zn isotopes to mineral dusts from the Chinese Loess Plateau in order to elucidate the main processes leading to Zn fractionation and affirmed that $\delta^{66/64}$Zn variations between loess and palaeosol are not sensitive to glacial–interglacial source fluctuations or wind sorting but could result from loess pedogenesis.

Biomonitoring

Zinc isotope composition of mollusc tissues have been proposed as a novel tool potentially capable of integrating sources, fates and bioavailability information of Zn contamination (Shiel *et al.* 2012, 2013; Petit *et al.* 2015; Araújo *et al.* 2021; Fig. 2). Metal concentrations in mollusc tissues is traditionally used in 'Mussel Watch' programmes in several countries to monitor the levels of contamination in coastal and marine ecosystems (Schöne and Krause 2016). Studies conducted with bivalves on the west coast in Canada showed homogeneous Zn isotope signatures that over-lapped those of unpolluted soils, sediments and marine water (Shiel *et al.* 2012). However, in the case of the Gironde estuary (a site historically impacted by metallurgy), the Zn isotopic signatures in the dissolved pool changes along the fluvial-estuarine due to successive adsorption processes in sediment particles along the Maximum Turbid Zone (MTZ) (Petit *et al.* 2015). In this case, the isotope records of oysters are close to isotope compositions of the dissolved Zn, besides indicating that particulate Zn is the main source of Zn to the oysters (Petit *et al.* 2015). Another recent study exposed oysters to waters with different isotopic signatures and concluded that Zn isotope ratios measured in oysters could be used for Zn source tracking (Ma *et al.* 2020). In contrast, bivalve molluscs collected in severely contaminated areas by electroplating wastes are not correlated to the sources identified in sediment samples, indicating that the isotope record of zinc in bivalve tissues may be controlled by additional factors such as speciation and bioavailability and bioaccumulation pathways via solution or particulate matter (Araújo *et al.* 2017).

Ma *et al.* (2020) measured Zn isotopes in molluscs at a hydrothermal vent to understand how the isotopic compositions can change in these organisms in an extreme environment where metal-enriched fluids are in contact with chemosymbiotic animals. Ma *et al.* (2020) did not observe a significant difference in $\delta^{66/64}$Zn among tissues of the molluscs analysed, suggesting the absence of Zn isotope fractionation during internal Zn transport. In addition, they concluded that different species exhibited different mechanisms of Zn uptake, related to different nutrient acquisition and different anatomical differences, which can be tracked by Zn isotopic compositions.

Zn isotopes may record this biological activity based on the preferential uptake of lighter Zn isotopes by phytoplankton/bacteria (John and Conway 2014). The uptake of different Zn isotopes by these microorganisms depends on the concentration of free ions in the nutrient solution (Desaulty *et al.* 2017). The uptake of heavy isotopes is favoured in low concentration solution. Furthermore, when the mechanism is diffuse transport across the membrane cell, the planktons tend to take up the lighter isotopes (John *et al.* 2007). Although numerous studies have explored the extent of Zn isotopic fractionations in controlled laboratory settings, only a limited number of field studies have utilized these findings to restrict the understanding of transfer mechanisms for these elements in real

environmental conditions, and because the interactions between metal and organisms are numerous and complex, there remain large gaps in understanding Zn transfer within the planktonic food web.

Zinc isotope system in dietary and metabolic processes

The isotopic composition of Zn in trophic levels is influenced by a combination of dietary sources, environmental conditions and physiological processes (Jaouen *et al.* 2013*a*; Fig. 2). By understanding how these factors can affect Zn isotopes, researchers can gain insights into the movement of Zn through food webs and the biogeochemical processes that underlie ecosystem functioning. The physiological processes of an organism can also influence the isotopic composition of Zn in its tissues. For example, different physiological processes such as absorption, assimilation and excretion can lead to isotopic fractionation. Additionally, the metabolic rate of an organism can also influence the isotopic composition of Zn in its tissues, as organisms with higher metabolic rates may have different Zn isotopic compositions than organisms with lower metabolic rates (Jaouen *et al.* 2016*a*, *b*).

The isotopic composition of Zn in an organism is largely determined by the isotopic composition of the food that it consumes. Different dietary sources may have different isotopic signatures, which can influence the isotopic composition of Zn in the organism. For example, plant-based diets may have different Zn isotopic compositions than diets consisting of animal products. Because of the large differences of $\delta^{66/64}$Zn values observed in the blood of vegetarians and compared with omnivores, the effects of the diet can be tracked in each group (Costas-Rodríguez *et al.* 2014; McCormack *et al.* 2022) In general, vegetables, cereals and derived products showed an enrichment of the heavier Zn isotopes, whereas a depletion is observed in products of animal origin (meat, fish, egg and semi-skimmed milk), relative to human blood samples. Thus, the lower $\delta^{66/64}$Zn values found in food products of animal origin appear to be reflected in the lower $\delta^{66/64}$Zn value observed in blood from an omnivorous population compared to that from a vegetarian population (Van Heghe *et al.* 2013; Costas-Rodríguez *et al.* 2014; McCormack *et al.* 2022). Beyond the dietary, correlations between Zn isotope compositions of blood with age are also found in the isolated population of Yakut (Jaouen *et al.* 2013*a*). This same sampling showed a discrepancy between the average $\delta^{66/64}$Zn value of blood between European and Japanese populations, which can be associated with different metabolic rates (Jaouen *et al.* 2013*a*).

The lighter $\delta^{66/64}$Zn values in the food of animal origin seems to reflect the isotope fractionation that takes place along the trophic chains. In African terrestrial food webs, $\delta^{66/64}$Zn values in both bone and dental enamel of carnivore animals are lighter by approximately 0.4–0.5‰ in comparison to bones and dental enamel of herbivores (Jaouen *et al.* 2013*b*). In the analysis of marine mammal bones (walruses, bearded seals, ringed seals and polar bears), the $\delta^{66/64}$Zn values of marine mammal bones also showed a trend toward lighter isotopic values with the increasing of trophic level (Jaouen *et al.* 2016*b*). However, different Zn isotope patterns are found in the terrestrial trophic chain of South Africa, where no significant Zn isotope fractionation is observed between bones of herbivores and bones of carnivores (including lion and hyena) (Jaouen *et al.* 2016*a*).

More studies regarding internal Zn isotope fractionation within animal bodies and the relationship between diet and bioavailability are necessary to understand how Zn isotopes fractionate from low to high trophic levels. For example, the tendency of heavier Zn isotope compositions of herbivores has been attributed to the precipitation of Zn with phytates in the intestine, inhibiting Zn absorption. This precipitation favours the binding of light Zn isotopes to the phytates, which implies that heavy Zn isotopes are more bioavailable (Jaouen *et al.* 2013*b*). In controlled feeding studies, it has been demonstrated

that for modern mammals, muscle tissue and bones have a different Zn isotope composition, where muscle tissue had ^{66}Zn-depleted values compared to the food ($\Delta^{66/64}$Zn$_{\text{muscles-food}} \approx -0.2$‰) and bone had ^{66}Zn-enriched values ($\Delta^{66/64}$Zn$_{\text{bones-food}} \approx 0.1$–$0.4$‰) (Jaouen *et al.* 2013*b*).

Investigations *in vivo* of Zn isotope ratios in mayflies (*Neocloeon triangulifer*) from larval to adult stages using biodynamic isotope models demonstrated significant isotope fractionation through the life stages of the insect. Upon metamorphosis to subimago, Zn losses are above 70%, accompanied by enrichment of heavier isotopes in the Zn pool remaining in the subimago bodies, whereas the Zn excess pool excreted along the time is isotopically light (Wanty *et al.* 2017). These results indicate the potential to use Zn isotope ratio information to infer internal distribution mechanisms and pathways in the cells and tissues of invertebrate organisms.

Over the past three years, $\delta^{66/64}$Zn values were used, combined with other stable isotopes (i.e. δ^{15}N, δ^{13}C; McCormack *et al.* 2021), in different mammal species from multiple Arctic archaeological sites in order to investigate trophic interactions between predator and prey over a broad geographical area, and it is concluded that $\delta^{66/64}$Zn analysis is the best tool to compare diets between spatially and temporally distinct locations. McCormack *et al.* (2022) demonstrated the use of Zn isotopes to assess the trophic level in diverse extant and extinct sharks, concluding that the δ^{66}Zn signature remains preserved in animal teeth, and furthermore, the differences between this signature among different species can be useful to elucidate the extinction cause of sharks.

Biomedicine

Interest in applying high-precision stable isotopic analysis in a biomedical context has increased significantly over the last 20 years (Mahan *et al.* 2020; Vanhaecke and Costas-Rodríguez 2021). The potential of metal stable isotopic analysis for understanding human diseases can be demonstrated *in vitro* using cell lines, *in vivo* using animal models, or in studies involving human subjects (Krayenbuehl *et al.* 2005; Aramendía *et al.* 2013; Resano *et al.* 2013; Sullivan *et al.* 2023). In these studies, samples are typically analysed that are minimally invasive to obtain (e.g. urine and blood fractions), with the hypothesis that changes in metal homeostasis that are associated with the disease pathology can cause differences in stable isotopic compositions elsewhere in the body that are detectable when compared with a suitably matched control group (Larner *et al.* 2015; Jaouen *et al.* 2019).

Due to the implication of Zn in numerous processes in the human body, an important focus has been revealing the influence of various lifestyle and physiological factors on Zn isotopic fractionation (Sullivan *et al.* 2023). Enhancing our knowledge of physiological and lifestyle factors that induce Zn isotopic fractionation in the human body allows for the appropriate control of confounding factors and is essential to resolving Zn isotopic signatures that are related to a particular disease pathology. In order to explore the applicability of Zn isotopes on understanding metal homeostasis and as a biomarker for diseases, Moynier *et al.* (2013) assessed the distribution of Zn isotopes in various mouse tissues and found that that most organs are isotopically distinct (Fig. 2). Moynier *et al.* (2013) observed that red blood cells and bones are enriched by ~0.5‰ in ^{66}Zn relative to ^{64}Zn when compared with serum, and around ~1‰ when compared with brain and liver, which is explained by the equilibrium isotopes between different bonding environments of Zn in different organs. Furthermore, differences in gender and genetic background did not affect the isotopic distribution of Zn.

There is strong evidence from animal model and human subject experiments that sex does not influence Zn isotopic compositions, and no difference has been found between the blood Zn isotopic

composition of menstruating and non-menstruating populations (Albarède *et al.* 2011; Jaouen *et al.* 2012, 2019; Moynier *et al.* 2013; Van Heghe *et al.* 2014; Mahan *et al.* 2018; Schilling *et al.* 2021). There is conflicting evidence on the influence of age, with some studies showing an increase in $\delta^{66/64}$Zn values with age and others showing none (Jaouen *et al.* 2013*a*; Van Heghe *et al.* 2014; Schilling *et al.* 2021; Sullivan *et al.* 2023). Studies of modern terrestrial food webs, experimental animals, and ancient and modern humans reveal that ^{64}Zn tends to be enriched up the trophic chain (Balter *et al.* 2010; Jaouen *et al.* 2013*b*, 2016*a*, *b*, 2017, 2020, 2022; Moynier *et al.* 2013). Human dietary components have also been shown to have distinct Zn isotopic signatures, with food from plant origin having a $\delta^{66/64}$Zn of 0.40 ± 0.42‰ (standard deviation, 1s) and food from animal origin having a $\delta^{66/64}$Zn of -0.34 ± 0.42‰ (1s) (Costas-Rodríguez *et al.* 2014). This is reflected in a difference between the δ^{66}Zn value of blood from omnivores (0.12 ± 0.07‰ (1σ), and that of lacto-ovo vegetarians (0.26 ± 0.04‰ (1σ) (Van Heghe *et al.* 2012; Costas-Rodríguez *et al.* 2014). A similar pattern is also found between the urine $\delta^{66/64}$Zn values of omnivores (0.19 ± 0.21‰ (1σ)) and both vegetarians (0.49 ± 0.27‰ (1σ) and dairy-free healthy humans (0.39 ± 0.19‰ (1σ) (Moore *et al.* 2019).

Several other physiological and lifestyle factors, including blood type, alcohol and caffeine consumption, smoking, postprandial effects and body mass index, have been investigated to ascertain whether they influence Zn isotopic compositions in the human body, but no effects have been demonstrated (Albarède *et al.* 2011; Van Heghe 2013; Moore *et al.* 2019; Sullivan *et al.* 2020). A number of factors remain to be investigated for their influence on bodily Zn isotopic compositions (e.g. vitamin and nutrient supplementation, basal metabolic rate, physical activity, wound healing and inflammation, pregnancy events, and natural and anthropogenic Zn exposure) (Sullivan *et al.* 2023).

When it comes to the study of Zn isotopic fractionation in the context of human disease, most investigations have focused on cancer (Larner *et al.* 2015; Hastuti *et al.* 2020*b*; Schilling *et al.* 2020, 2021, 2022; Sullivan *et al.* 2021), although several have studied neurological conditions, such as amyotrophic lateral sclerosis (ALS) and Alzheimer's disease (AD) (Moynier *et al.* 2017, 2020; Sauzéat *et al.* 2018). Zinc isotopes have also been applied to monitor homeostatic changes following bariatric surgery, with the difference between the $\delta^{66/64}$Zn values in serum and whole blood becoming larger over the post-operative time (from 3 to 6 to 12 months), and this is suggested to reflect disrupted Zn homeostasis, impaired Zn status and/or reduced Zn absorption capacity in bariatric surgery patients (Hastuti *et al.* 2020*a*). Another study also investigated whether Zn status can be assessed using the Zn isotope composition of urine and found that samples with lower Zn concentrations are systematically enriched in ^{66}Zn (Moore *et al.* 2019). In the context of neurological disorders, no difference was found between the Zn isotopic composition of cerebrospinal fluid (CSF) from individuals with ALS and controls, but CSF from individuals with AD tends to have slightly lower $\delta^{66/64}$Zn values than controls (Sauzéat *et al.* 2018). This may be explained by results from two other studies that found the accumulation of the heavy isotope of Zn in the brains of humans with AD and APPswe/ PSEN1dE9 (model of AD) mice compared with the brains of controls (Moynier *et al.* 2017, 2020).

In the context of cancer, most focus has been spent on studying the potential of Zn isotopic compositions as a diagnostic marker in blood fractions and urine (Larner *et al.* 2015; Hastuti *et al.* 2020*b*; Schilling *et al.* 2020, 2021). The Zn isotopic composition of the tumours that would likely influence any Zn isotopic fractionation in blood and urine has only been determined in two studies to date (Larner *et al.* 2015; Sullivan *et al.* 2021). Interestingly, despite a statistically significant decrease in $\delta^{66/64}$Zn being found in breast cancer tumours compared with histologically normal tissue adjacent

to tumours (NAT), this is accompanied by no change in $\delta^{66/64}$Zn values in the urine of individuals with breast cancer relative to controls (Schilling *et al.* 2021; Sullivan *et al.* 2021). Paradoxically, a similar statistically significant decrease in $\delta^{66/64}$Zn that is found in benign breast tumours compared to NAT is accompanied by a statistically significant decrease in the urine $\delta^{66/64}$Zn values of individuals with benign breast disease relative to controls (Schilling *et al.* 2021; Sullivan *et al.* 2021). Urine from prostate and pancreatic cancer is also characterized by the relative enrichment of ^{64}Zn compared with controls (Schilling *et al.* 2020, 2021). In the case of haematological malignancy (HM), Zn concentrations and Zn isotopic compositions determined in the blood plasma of individuals with HM are significantly different from controls (Hastuti *et al.* 2020*b*). Interestingly, this is the only instance of a blood fraction or urine having a heavier Zn isotopic composition than in controls. The prognostic potential of Zn isotopic composi-tions was demonstrated using time-dependent receiver operating characteristic curves, with plasma $\delta^{66/64}$Zn values showing a similar area under the curve to creatinine, a prognostic marker of HM (Hastuti *et al.* 2020*b*).

One key area requiring additional attention for the advancement of Zn isotopic analysis in a biomedical context is the understanding of Zn isotopic fractionation mechanisms. Much of our current understanding of Zn isotopic fractionation in a biomedical context comes from density functional theory estimation of Zn isotopic fractionation that generally predicts the increasing enrichment of ^{66}Zn when binding to increasingly electronegative ligands in amino acids (Fujii *et al.* 2014). For example, Zn bound to cysteine (Zn–S bonds) is expected to be more enriched in ^{64}Zn than in Zn bound to the histidine (Cu–N bonds). However, it is not yet possible to predict Zn isotopic fractionation in more complex molecules, such as proteins. The further characterization of Zn isotopic compositions of cancerous tumours will also aid the understanding of fractionation mechanisms. To that end, a recent study performed Zn uptake-efflux experiments with a human breast cancer cell line (model for triple receptor negative breast cancer, MDA-MB-231) using a drip-flow reactor (Schilling *et al.* 2022). Zinc isotopic fractionation is in the opposite direction to what is expected from the measurement of breast cancer tumours, with cell uptake showing an enrichment of ^{66}Zn compared to cell efflux (Schilling *et al.* 2022). This research highlights the differences that can occur between *in vitro* and *in vivo* results and demonstrates that much work is needed to understand Zn homeostasis and isotopic fractionation in the context of cancer (Schilling *et al.* 2022).

Source tracking

Anthropogenic sources

Given the evidence of variable Zn isotope ratios in environmental compartments (i.e. low-temperature biogeochemical processes, geogenic processes and in ore-refining industries), Zn isotopic signature differences provide a way to discern the sources, pathways and sinks of pollutants (natural and anthropogenic), as well as transfer mechanisms between abiotic and biotic compartments (Tonhá *et al.* 2020). In the past decade, Zn isotopes have been proven useful as an environmental tool to track contaminant sources in contaminated soils (Fekiacova *et al.* 2015), sediment cores (Thapalia *et al.* 2015), coastal environments (Tonhá *et al.* 2020), bivalves (Araújo *et al.* 2017) and river surface waters (Chen *et al.* 2008).

In a series of studies conducted in Sepetiba Bay (Rio de Janeiro, Brazil), a site historically impacted by metallurgy activity, spatial and temporal analysis of Zn isotope compositions of sediment and rock samples fits well in a model of mixing between three main end-members: (i) continental materials brought via rivers; (ii) marine

sources; and (iii) a major anthropogenic source associated with the old electroplating wastes released into the bay (Araújo *et al.* 2017, 2018). Sediment cores collected in the mud flat showed a high correlation between Zn isotope compositions and Zn enrichment factors, suggesting (i) good preservation of isotope records of natural and anthropogenic sources and (ii) no significant isotope fractionation during sediment transport or as a result of diagenetic reactions post-deposition in the estuarine system. The sediment core sampled from a mangrove located in the zone impacted by the old electroplating activity presented levels of Zn up to 4% (dry weight) and preserved the isotope signatures of electroplating wastes. However, there is evidence that biogeochemical processes triggered by hydrodynamics, bioturbation or rhizosphere processes slightly changed the isotope signatures in some layers.

Desaulty *et al.* (2017) collected surface water and sediments from a French river close to a wastewater treatment plant (WWTP) in order to establish the influence of this anthropogenic source on the river catchment area. The results showed that even several kilometres downstream from the WWTP, Zn could still be determined relative to this anthropogenic source. Desaulty *et al.* (2017) also established a correlation between the low clay mineral content and the low adsorption on sediments relative to the distance from the source. Zinc isotopes are also used in different environments to establish source relationships. Xia *et al.* (2020) revealed Zn sources and transport processes in a karst region by analysing tailings, river waters, sediment, dust and soil in southwestern China. The study was successful in tracking the pollution sources and pathways of heavy metals in this complicated hydrosystem, showing distinct Zn isotope compositions among tailings, agriculture and geogenic soil.

We conclude that besides being a successful tool to analyse different sources, Zn isotopic interpretation may be challenging due to the numerous sources of Zn in the environment. Combined isotopic systems can take us further on understanding the behaviour of trace metals in the different compartments of a river basin by tracking different physical and chemical processes governing the distribution of solid and dissolved phases.

Urban sources: road dust and traffic-related emissions

Providing isotope data from various anthropogenic sources remains an essential task for source identification in environmental forensic fields and estimating their contributions. For example, non-exhaust emission (NEE) sources (e.g. brake pads, tires, road paints, asphalt and curbs) are considered as significant anthropogenic sources in the urban environment with their distinct isotope signatures (Dong *et al.* 2017; Jeong 2022; Jeong *et al.* 2022). Isotope compositions of traffic-related NEE sources covered from –0.4 to 0.6‰ ($\delta^{66/64}$Zn) (Jeong 2022; Jeong *et al.* 2022), and of road dust ranged from –0.1 to 0.4‰ (Dong *et al.* 2017; Souto-Oliveira *et al.* 2018; Jeong and Ra 2021) (converted value by adding 0.30‰ from IRMM-3702 to JMC-Lyon; Moynier *et al.* 2017). Ultimately, it is imperative to prioritize the effective management of traffic-related pollutants, as these contaminants can traverse from terrestrial sources to the vast expanses of the ocean, where they can exert deleterious effects on marine life. As humans ingest marine food resources, the ramifications of this contamination have the potential to extend to human health. Hence, a concerted effort towards mitigating and preventing such pollutants is critical for safeguarding the sustainability of marine ecosystems and the welfare of humankind.

Antifouling paints

Antifouling paints are widely employed to protect submerged surfaces against biofouling, which is the attachment and growth of marine organisms on submerged surfaces such as boat hulls and pipelines, leading to detrimental effects on economic and operational aspects. Following the ban of tributyltin (TBT), Cu-based antifouling paints have emerged as viable alternatives for preventing biofouling. However, concerns regarding their potential environmental impact have been raised due to their extremely high concentrations of Cu and Zn (Jeong *et al.* 2023). The Zn isotopic composition ($\delta^{66/64}$Zn) of antifouling paints ranged from –0.04 to 0.33‰ (mean: 0.17 ± 0.20‰, 2σ, $n = 25$; Jeong *et al.* 2023) (converted value by adding 0.30‰ from IRMM-3702 to JMC-Lyon; Moynier *et al.* 2017), and their chemical compositions indicate that they are distinguished from the other urban sources.

Metallurgical waste

The isotope signatures of feed ores and coals have important implications to final products and byproducts produced in metallurgic industry and coal-fired power plants. High-temperature processes employed during sulfide ore smelting and coal combustion induce significant isotope fractionation, with lighter Zn isotopes entering the vapour phase and leaving the residual material (e.g. fly ash particles, slags) enriched with the heavier isotopes by Rayleigh fractionation processes (Sivry *et al.* 2008; Borrok *et al.* 2010; Ochoa Gonzalez and Weiss 2015; Yin *et al.* 2015). In the case of ore refining, additional electroplating steps also seem to affect Zn isotope fractionation, as demonstrated in controlled electrochemical experiments (Kavner *et al.* 2008; Black *et al.* 2011) and in the analysis of contaminated sediment by electroplating slags. Despite these gaps concerning the electrochemistry effects on industrial plants, a general trend has been observed in Zn extraction of sulfide ores: the production of air emissions with the lightest signatures ($\delta^{66/64}$Zn = -0.66‰), slags with the heaviest signatures ($\delta^{66/64}$Zn = 1.49‰) and final products (refined Zn electroplated materials) with isotope compositions close to the ores ($\delta^{66/64}$Zn = 0.22‰) (Yin *et al.* 2015). The significant differences in the isotope compositions derived of anthropogenic sources compared to the natural background (soils and rocks, for example) have allowed the use of Zn isotopes as a powerful tracer of sources capable of discriminating and quantifying several pollutant sources concerning mining and metallurgy byproducts (Dolgopolova *et al.* 2006; Weiss *et al.* 2007; Sivry *et al.* 2008; Mattielli *et al.* 2009), and others such as vehicle emissions and tire wear (Gioia *et al.* 2008; Thapalia *et al.* 2015; Souto-Oliveira *et al.* 2018, 2019), and wastewaters and sewage (Chen *et al.* 2008, 2009*a*, *b*).

Conclusions

The versatility and usefulness of Zn isotopes is proved by the many applications in different scientific fields. The current increase of research groups on metal isotope biogeochemistry will contribute to the continuous developing of the Zn isotope biogeochemistry, leading to new methodologies and advances in the theoretical understanding about the factors that control its isotope fractionation. The isotope determinations combined with Zn speciation are an important step forward to the understanding of biogeochemical and environmental cycles, and can open new frontiers in biomedicine applications, including the establishment of the medical isotope metallomics field.

Future studies are required to link Zn speciation and bioavailability and mechanisms of isotope fractionation during its incorporation in biota or partitioning within higher organisms or the human body. The development of selective or sequential extraction for isotope analysis of different phases of soils and sediments could be a helpful auxiliary tool for comprehending the isotope fractionation that occurs during bioaccumulation. However, more robust and reproducible protocols, beyond the verification of possible artefacts associated with the chemical procedure, are also required.

New efforts to increase the assessment of Zn isotopic signatures in environmental compartments can contribute to identify sources and sinks of anthropogenic Zn and its cycling through the biogeosphere, in either the local or global scale. Of special concern for aquatic systems is the analysis of the pore waters, which has important implications for understanding diagenetic reactions and bioavailability of Zn, mainly in coastal zones and wetlands, where the large gradients of redox conditions promote periodic releasing and trapping of metal in sediments.

In biomonitoring studies, more tests using other species must be encouraged to verify the feasibility of Zn isotopes as a monitor of metal contamination. To date, their use in bivalve molluscs has been hampered by the lack of knowledge about the physiological influences on the Zn bio-isotope record. Finally, new controlled experiments regarding the effects of chemistry coordination of Zn with different ligands will be useful to interpret and predict the isotope fractionation in the environment and biological systems, encompassing stratigraphic Zn profiles along the geological time to cellular metabolism processes. Although Zn isotopes as source trackers have been intensively studied in the past years, most studies have mainly focused on tracing point-source pollutions in the nearby environment instead of studying it on a large scale, i.e. in the case of aquatic environments, a combination of hydrodynamical processes (i.e. discharge, mixing between tributaries). The understanding of the metal behaviour demands long-term and high-resolution monitoring of metal loads.

This review gathers information on different applications of Zn isotopes in different types of materials and environments. Understanding and implementing these isotopic signatures will enhance our capacity to interpret findings and conduct routine, highly accurate and precise measurements of the Zn isotope ratio in diverse types of samples. This advancement opens avenues for new and exciting applications.

Scientific editing by Scott Wood

Author contributions **TPJ**: conceptualization (lead), data curation (lead), formal analysis (lead), investigation (lead), methodology (lead), validation (lead), writing – original draft (lead); **BV**: data curation (lead), formal analysis (lead), funding acquisition (lead), investigation (lead), methodology (lead), writing – original draft (lead); **MIL**: conceptualization (lead), investigation (lead), supervision (lead), validation (lead), writing – original draft (lead); **ALH**: conceptualization (lead), data curation (lead), investigation (lead), methodology (lead), supervision (lead), validation (lead), writing – original draft (lead); **KVS**: conceptualization (lead), investigation (equal), validation (equal), writing – original draft (lead); **HJ**: conceptualization (equal), investigation (equal), validation (equal), writing – original draft (equal); **DFA**: data curation (lead), formal analysis (lead), investigation (lead), methodology (lead), writing – original draft (lead).

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

References

Adriano, D.C. 2001. *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals*, **860**. Springer, New York, https://doi.org/10.1007/978-0-387-21510-5

Ahlf, W., Drost, W. and Heise, S. 2009. Incorporation of metal bioavailability into regulatory frameworks – metal exposure in water and sediment. *Journal of Soils and Sediments*, **9**, 411–419, https://doi.org/10.1007/s11368-009-0109-6

Albarède, F. 2004. The stable isotope geochemistry of copper and zinc. *Reviews in Mineralogy and Geochemistry*, **55**, 409–427, https://doi.org/10.2138/gsrmg.55.1.409

Albarède, F. 2008. *Geochemistry, An Introduction*. 2nd edn, Cambridge University Press, https://doi.org/10.1017/CBO9780511807435

Albarède, F. 2015. Metal stable isotopes in the human body: a tribute of geochemistry to medicine. *Elements*, **11**, 265–269, https://doi.org/10.2113/gselements.11.4.265

Albarède, F. and Beard, B. 2004. Analytical methods for non-traditional isotopes. *Reviews in Mineralogy and Geochemistry*, **55**, 113–152, https://doi.org/10.2138/gsrmg.55.1.113

Albarède, F., Télouk, P., Lamboux, A., Jaouen, K. and Balter, V. 2011. Isotopic evidence of unaccounted for Fe and Cu erythropoietic pathways. *Metallomics*, **3**, 926–933, https://doi.org/10.1039/C1MT00025J

Albarède, F., Télouk, P. and Balter, V. 2017. Medical applications of isotope metallomics. *Reviews in Mineralogy and Geochemistry*, **82**, 851–885, https://doi.org/10.2138/rmg.2017.82.20

Andersen, M.B., Vance, D. *et al.* 2011. The Zn abundance and isotopic composition of diatom frustules, a proxy for Zn availability in ocean surface seawater. *Earth and Planetary Science Letters*, **301**, 137–145, https://doi.org/10.1016/j.epsl.2010.10.032

Andreini, C., Banci, L., Bertini, I. and Rosato, A. 2006. Counting the zinc-proteins encoded in the human genome. *Journal of Proteome Research*, **5**, 196–201, https://doi.org/10.1021/pr050361j

Aramendía, M., Rello, L., Resano, M. and Vanhaecke, F. 2013. Isotopic analysis of Cu in serum samples for diagnosis of Wilson's disease: a pilot study. *Journal of Analytic Atomic Spectrometry*, **28**, 675–681, https://doi.org/10.1039/C3JA30349G

Araújo, D., Machado, W. *et al.* 2017. A critical examination of the possible application of zinc stable isotope ratios in bivalve mollusks and suspended particulate matter to trace zinc pollution in a tropical estuary. *Environmental Pollution*, **226**, 41–47, https://doi.org/10.1016/j.envpol.2017.04.011

Araújo, D.F., Machado, W., Weiss, D., Mulholland, D.S., Garnier, J., Souto-Oliveira, C.E. and Babinski, M. 2018. Zinc isotopes as tracers of anthropogenic sources and biogeochemical processes in contaminated mangroves. *Applied Geochemistry*, **95**, 25–32, https://doi.org/10.1016/j.apgeochem.2018.05.008

Araújo, D.F., Ponzevera, E. *et al.* 2019. Assessment of the metal contamination evolution in the Loire estuary using Cu and Zn stable isotopes and geochemical data in sediments. *Marine Pollution Bulletin*, **143**, 12–23, https://doi.org/10.1016/j.marpolbul.2019.04.034

Araújo, D.F., Ponzevera, E. *et al.* 2021. Application of Zn isotope compositions in oysters to monitor and quantify anthropogenic Zn bioaccumulation in marine environments over four decades: a 'mussel watch program' upgrade. *Environmental Sciences & Technology- Water*, **1**, 1035–1046, https://doi.org/10.1021/acsestwater.1c00010

Archer, C. and Vance, D. 2004. Mass discrimination correction in multiple-collector plasma source mass spectrometry: an example using Cu and Zn isotopes. *Journal of Analytical Atomic Spectrometry*, **19**, 656–665, https://doi.org/10.1039/b315853e

Archer, C., Andersen, M.B. *et al.* 2017. Inter-calibration of a proposed new primary reference standard AA-ETH Zn for zinc isotopic analysis. *Journal of Analytical Atomic Spectrometry*, **32**, 415–419, https://doi.org/10.1039/C6JA00282J

Arnold, R.D. and Wade, J.P. 2015. A definition of systems thinking: a systems approach. *Procedia Computer Science*, **44**, 669–678, https://doi.org/10.1016/j.procs.2015.03.050

Arnold, T., Schönbächler, M. *et al.* 2010. Measurement of zinc stable isotope ratios in biogeochemical matrices by double-spike MC-ICPMS and determination of the isotope ratio pool available for plants from soil. *Analytical and Bioanalytical Chemistry*, **398**, 3115–3125, https://doi.org/10.1007/s00216-010-4231-5

Aucour, A.M., Bedell, J.P., Queyron, M., Tholé, R., Lamboux, A. and Sarret, G. 2017. Zn speciation and stable isotope fractionation in a contaminated urban wetland soil–Typha latifolia system. *Environmental Science & Technology*, **51**, 8350–8358, https://doi.org/10.1021/acs.est.6b02734

Balistrieri, L.S., Borrok, D.M., Wanty, R.B. and Ridley, W.I. 2008. Fractionation of Cu and Zn isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: experimental mixing of acid rock drainage and ambient river water. *Geochimica et Cosmochimica Acta*, **72**, 311–328, https://doi.org/10.1016/j.gca.2007.11.013

Balter, V., Zazzo, A., Moloney, A.P., Moynier, F., Schmidt, O., Monahan, F.J. and Albarède, F. 2010. Bodily variability of zinc natural isotope abundances in sheep. *Rapid Communications in Mass Spectrometry*, **24**, 605–612, https://doi.org/10.1002/rcm.4425

Becker, J.S. 2005. Recent developments in isotope analysis by advanced mass spectrometric techniques: plenary lecture. *Journal of Analytical Atomic Spectrometry*, **20**, 1173, https://doi.org/10.1039/b508895j

Bermin, J., Vance, D., Archer, C. and Statham, P.J. 2006. The determination of the isotopic composition of Cu and Zn in seawater. *Chemical Geology*, **226**, 280–297, https://doi.org/10.1016/j.chemgeo.2005.09.025

Bianchi, F., Maffini, M., Mangia, A., Marengo, E. and Mucchino, C. 2007. Experimental design optimization for the ICP-AES determination of Li, Na, K, Al, Fe, Mn and Zn in human serum. *Journal of Pharmaceutical and Biomedical Analysis*, **43**, 659–665, https://doi.org/10.1016/j.jpba.2006.07.054

Bigalke, M., Weyer, S., Kobza, J. and Wilcke, W. 2010. Stable Cu and Zn isotope ratios as tracers of sources and transport of Cu and Zn in contaminated soil. *Geochimica et Cosmochimica Acta*, **74**, 6801–6813, https://doi.org/10.1016/j.gca.2010.08.044

Black, J.R., Kavner, A. and Schauble, E.A. 2011. Calculation of equilibrium stable isotope partition function ratios for aqueous zinc complexes and metallic zinc. *Geochimica et Cosmochimica Acta*, **75**, 769–783, https://doi.org/10.1016/j.gca.2010.11.019

Borrok, D.M., Wanty, R.B., Ridley, W.I., Wolf, R., Lamothe, P.J. and Adams, M. 2007. Separation of copper, iron, and zinc from complex aqueous solutions for isotopic measurement. *Chemical Geology*, **242**, 400–414, https://doi.org/10.1016/j.chemgeo.2007.04.004

Borrok, D.M., Nimick, D.A., Wanty, R.B. and Ridley, W.I. 2008. Isotopic variations of dissolved copper and zinc in stream waters affected by historical mining. *Geochimica et Cosmochimica Acta*, **72**, 329–344, https://doi.org/10.1016/j.gca.2007.11.014

Borrok, D.M., Gieré, R., Ren, M. and Landa, E.R. 2010. Zinc isotopic composition of particulate matter generated during the combustion of coal and coal + tire-derived fuels. *Environmental Science & Technology*, **44**, 9219–9224, https://doi.org/10.1021/es102439g

Bridgestock, L.J., Williams, H. *et al.* 2014. Unlocking the zinc isotope systematics of iron meteorites. *Earth and Planetary Science Letters*, **400**, 153–164, https://doi.org/10.1016/j.epsl.2014.05.029

Brown, G.E. and Calas, G. 2011. Environmental mineralogy – understanding element behavior in ecosystems. *Comptes Rendus Geoscience*, **343**, 90–112, https://doi.org/10.1016/j.crte.2010.12.005

Bryan, A.L., Dong, S., Wilkes, E.B. and Wasylenki, L.E. 2015. Zinc isotope fractionation during adsorption onto Mn oxyhydroxide at low and high ionic strength. *Geochimica et Cosmochimica Acta*, **157**, 182–197, https://doi.org/10.1016/j.gca.2015.01.026

Bullen, T.D. and Eisenhauer, A. 2009. Metal stable isotopes in low-temperature systems: a primer. *Elements*, **5**, 349–352, https://doi.org/10.2113/gselements.5.6.349

Bullen, T.D. and Walczyk, T. 2009. Environmental and biomedical applications of natural metal stable isotope variations. *Elements*, **5**, 381–385, https://doi.org/10.2113/gselements.5.6.381

Caldelas, C. and Weiss, D.J. 2017. Zinc homeostasis and isotopic fractionation in plants: a review. *Plant and Soil*, **411**, 17–46, https://doi.org/10.1007/s11104-016-3146-0

Caldelas, C., Dong, S., Araus, J.L. and Weiss, D.J. 2011. Zinc isotopic fractionation in *Phragmites australis* in response to toxic levels of zinc. *Journal of Experimental Botany*, **62**, 2169–2178, https://doi.org/10.1093/jxb/erq414

Chapman, J.B., Mason, T.F.D., Weiss, D.J., Coles, B.J. and Wilkinson, J.J. 2006. Chemical separation and isotopic variations of Cu and Zn from five geological reference materials. *Geostandards And Geoanalytical Research*, **30**, 5–16, https://doi.org/10.1111/j.1751-908X.2006.tb00907.x

Chasapis, C.T., Spiliopoulou, C.A., Loutsidou, A.C. and Stefanidou, M.E. 2012. Zinc and human health: an update. *Archives of Toxicology*, **86**, 521–534, https://doi.org/10.1007/s00204-011-0775-1

Chen, J., Gaillardet, J. and Louvat, P. 2008. Zinc isotopes in the Seine River waters, France: a probe of anthropogenic contamination. *Environmental Science & Technology*, **42**, 6494–6501, https://doi.org/10.1021/es800725z

Chen, J.B., Louvat, P., Gaillardet, J. and Birck, J.L. 2009*a*. Direct separation of Zn from dilute aqueous solutions for isotope composition determination using multi-collector ICP-MS. *Chemical Geology*, **259**, 120–130, https://doi.org/10.1016/j.chemgeo.2008.10.040

Chen, J., Gaillardet, J., Louvat, P. and Huon, S. 2009*b*. Zn isotopes in the suspended load of the Seine River, France: isotopic variations and source determination. *Geochimica et Cosmochimica Acta*, **73**, 4060–4076, https://doi.org/10.1016/j.gca.2009.04.017

Chen, H., Savage, P.S., Teng, F.Z., Helz, R.T. and Moynier, F. 2013. Zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth. *Earth and Planetary Science Letters*, **369–370**, 34–42, https://doi.org/10.1016/j.epsl.2013.02.037

Clearwater, S.J., Farag, A.M. and Meyer, J.S. 2002. Bioavailability and toxicity of dietborne copper and zinc to fish. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology*, **132**, 269–313, https://doi.org/10.1016/S1532-0456(02)00078-9

Cloquet, C., Carignan, J., Lehmann, M.F. and Vanhaecke, F. 2008. Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: a review. *Analytical and Bioanalytical Chemistry*, **390**, 451–463, https://doi.org/10.1007/s00216-007-1635-y

Conway, T.M. and John, S.G. 2014. The biogeochemical cycling of zinc and zinc isotopes in the North Atlantic Ocean. *Global Biogeochemical Cycles*, **28**, 1111–1128, https://doi.org/10.1002/2014GB004862

Conway, T.M., Rosenberg, A.D., Adkins, J.F. and John, S.G. 2013. A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. *Analytica Chimica Acta*, **793**, 44–52, https://doi.org/10.1016/j.aca.2013.07.025

Conway, T.M., Horner, T.J., Plancherel, Y. and González, A.G. 2021. A decade of progress in understanding cycles of trace elements and their isotopes in the oceans. *Chemical Geology*, **580**, 120381, https://doi.org/10.1016/j.chemgeo.2021.120381

Costas-Rodríguez, M., Van Heghe, L. and Vanhaecke, F. 2014. Evidence for a possible dietary effect on the isotopic composition of Zn in blood via isotopic

analysis of food products by multi-collector ICP-mass spectrometry. *Metallomics: Integrated Biometal Science*, **6**, 139–146, https://doi.org/10.1039/c3mt00244f

Couder, E., Mattielli, N. *et al.* 2015. Transpiration flow controls Zn transport in Brassica napus and Lolium multiflorum under toxic levels as evidenced from isotopic fractionation. *Comptes Rendus Géoscience*, **347**, 386–396, https://doi.org/10.1016/j.crte.2015.05.004

Cruz, K.J.C., de Oliveira, A.R.S. and do Nascimento Marreiro, D. 2015. Antioxidant role of zinc in diabetes mellitus. *World Journal of Diabetes*, **6**, 333, https://doi.org/10.4239/wjd.v6.i2.333

Dekov, V.M., Vanlierde, E. *et al.* 2014. Ferrihydrite precipitation in groundwater-fed river systems (Nete and Demer river basins, Belgium): insights from a combined Fe-Zn-Sr-Nd-Pb-isotope study. *Chemical Geology*, **386**, 1–15, https://doi.org/10.1016/j.chemgeo.2014.07.023

Deng, T.H.B., Cloquet, C. *et al.* 2014. Nickel and zinc isotope fractionation in hyperaccumulating and nonaccumulating plants. *Environmental Science & Technology*, **48**, 11926–11933, https://doi.org/10.1021/es5020955

Desaulty, A.-M. and Petelet-Giraud, E. 2020. Zinc isotope composition as a tool for tracing sources and fate of metal contaminants in rivers. *Science of the Total Environment*, **728**, 138599, https://doi.org/10.1016/j.scitotenv.2020.138599

Desaulty, A.M., Méheut, M., Guerrot, C., Berho, C. and Millot, R. 2017. Coupling DGT passive samplers and multi-collector ICP-MS: a new tool to measure Pb and Zn isotopes composition in dilute aqueous solutions. *Chemical Geology*, **450**, 122–134, https://doi.org/10.1016/j.chemgeo.2016.12.023

Ding, Z., Han, G., Qu, R., Liu, J. and Wang, P. 2024. Review on zinc isotopes in river systems: distribution and application. *Water*, **16**, 87, https://doi.org/10.3390/w16010087

Dolgopolova, A., Weiss, D.J., Seltmann, R., Kober, B., Mason, T.F.D., Coles, B. and Stanley, C.J. 2006. Use of isotope ratios to assess sources of Pb and Zn dispersed in the environment during mining and ore processing within the Orlovka-Spokoinoe mining site (Russia). *Applied Geochemistry*, **21**, 563–579, https://doi.org/10.1016/j.apgeochem.2005.12.014

Dong, S. and Wasylenki, L.E. 2016. Zinc isotope fractionation during adsorption to calcite at high and low ionic strength. *Chemical Geology*, **447**, 70–78, https://doi.org/10.1016/j.chemgeo.2016.10.031

Dong, S., Gonzalez, R.O., Harrison, R.M., Green, D., North, R., Fowler, G. and Weiss, D. 2017. Isotopic signatures suggest important contributions from recycled gasoline, road dust and non-exhaust traffic sources for copper, zinc and lead in PM10 in London, United Kingdom. *Atmospheric Environment*, **165**, 88–98, https://doi.org/10.1016/j.atmosenv.2017.06.020

Fekiacova, Z., Cornu, S. and Pichat, S. 2015. Tracing contamination sources in soils with Cu and Zn isotopic ratios. *Science of the Total Environment*, **517**, 96–105, https://doi.org/10.1016/j.scitotenv.2015.02.046

Fernandez, A. and Borrok, D.M. 2009. Fractionation of Cu, Fe, and Zn isotopes during the oxidative weathering of sulfide-rich rocks. *Chemical Geology*, **264**, 1–12, https://doi.org/10.1016/j.chemgeo.2009.01.024

Frassinetti, S., Bronzetti, G.L., Caltavuturo, L., Cini, M. and Della Croce, C. 2006. The role of zinc in life: a review. *Journal of Environmental Pathology, Toxicology and Oncology*, **25**, https://doi.org/10.1615/JEnvironPatholToxicolOncol.v25.i3.40

Fujii, T., Moynier, F., Blichert-Toft, J. and Albarède, F. 2014. Density functional theory estimation of isotope fractionation of Fe, Ni, Cu, and Zn among species relevant to geochemical and biological environments. *Geochimica et Cosmochimica Acta*, **140**, 553–576, https://doi.org/10.1016/j.gca.2014.05.051

Gaillardet, J., Viers, J. and Dupré, B. 2013. Trace elements in river waters. *In*: Holland, H.D. and Turekian, K.K. (eds) *Treatise on Geochemistry*. 2nd edn, Elsevier, 195–235, https://doi.org/10.1016/B978-0-08-095975-7.00507-6

Garçon, M., Sauzeat, L., Carlson, R.W., Shirey, S.B., Simon, M., Balter, V. and Boyet, M. 2017. Nitrile, latex, neoprene and vinyl gloves: a primary source of contamination for trace element and Zn isotopic analyses in geological and biological samples. *Geostandards and Geoanalytical Research*, **41**, 367–380, https://doi.org/10.1111/ggr.12161

Gélabert, A., Pokrovsky, O.S., Viers, J., Schott, J., Boudou, A. and Feurtet-Mazel, A. 2006. Interaction between zinc and freshwater and marine diatom species: surface complexation and Zn isotope fractionation. *Geochimica et Cosmochimica Acta*, **70**, 839–857, https://doi.org/10.1016/j.gca.2005.10.026

Gill, R. 1997. *Modern Analytical Geochemistry, An Introduction to Quantitative Chemical Analysis for Earth, Environmental and Materials Scientists*. Routledge, https://doi.org/10.4324/9781315844381

Gioia, S., Weiss, D., Coles, B., Arnold, T. and Babinski, M. 2008. Accurate and precise zinc isotope ratio measurements in urban aerosols. *Analytical Chemistry*, **80**, 9776–9780, https://doi.org/10.1021/ac8019587

Gu, J., Cui, P., Zeng, Z., Sun, Y., Sun, Q. and Wang, Y. 2022. Isotopic fractionation of Zn during soil sorption as influenced by soil properties and the Zn–O bond distance: insights from EXAFS and MC-ICP-MS. *Applied Geochemistry*, **145**, 105427, https://doi.org/10.1016/j.apgeochem.2022.105427

Guinoiseau, D., Gelabert, A., Moreau, J., Louvat, P. and Benedetti, M.F. 2016. Zn isotope fractionation during sorption onto kaolinite. *Environmental Science & Technology*, **50**, 1844–1852, https://doi.org/10.1021/acs.est.5b05347

Guinoiseau, D., Gélabert, A., Allard, T., Louvat, P., Moreira-Turcq, P. and Benedetti, M.F. 2017. Zinc and copper behaviour at the soil-river interface: new insights by Zn and Cu isotopes in the organic-rich Rio Negro basin.

Geochimica et Cosmochimica Acta, **213**, 178–197, https://doi.org/10.1016/j.gca.2017.06.030

Guinoiseau, D., Bouchez, J., Gélabert, A., Louvat, P., Moreira-Turcq, P., Filizola, N. and Benedetti, M.F. 2018. Fate of particulate copper and zinc isotopes at the Solimões-Negro river confluence, Amazon Basin, Brazil. *Chemical Geology*, **489**, 1–15, https://doi.org/10.1016/j.chemgeo.2018.05.004

Haase, H. and Rink, L. 2014. Multiple impacts of zinc on immune function. *Metallomics*, **6**, 1175–1180, https://doi.org/10.1039/c3mt00353a

Hambidge, K.M., Miller, L.V., Westcott, J.E., Sheng, X. and Krebs, N.F. 2010. Zinc bioavailability and homeostasis. *The American Journal of Clinical Nutrition*, **91**, 1478S–1483S, https://doi.org/10.3945/ajcn.2010.28674I

Hastuti, A.A.M.B., Costas-Rodríguez, M., Anoshkina, Y., Parnall, T., Madura, J.A. and Vanhaecke, F. 2020a. High-precision isotopic analysis of serum and whole blood Cu, Fe and Zn to assess possible homeostasis alterations due to bariatric surgery. *Analytical and Bioanalytical Chemistry*, **412**, 727–738, https://doi.org/10.1007/s00216-019-02291-2

Hastuti, A.A.M.B., Costas-Rodríguez, M., Matsunaga, A., Ichinose, T., Hagiwara, S., Shimura, M. and Vanhaecke, F. 2020b. Cu and Zn isotope ratio variations in plasma for survival prediction in hematological malignancy cases. *Scientific Reports*, **10**, 1–12, https://doi.org/10.1038/s41598-020-71764-7

He, Z., Archer, C., Yang, S. and Vance, D. 2023. Sedimentary cycling of zinc and nickel and their isotopes on an upwelling margin: implications for oceanic budgets and paleoenvironment proxies. *Geochimica et Cosmochimica Acta*, **343**, 84–97, https://doi.org/10.1016/j.gca.2022.12.026

Herzog, G.F., Moynier, F., Albarède, F. and Berezhnoy, A.A. 2009. Isotopic and elemental abundances of copper and zinc in lunar samples, Zagami, Pele's hairs, and a terrestrial basalt. *Geochimica et Cosmochimica Acta*, **73**, 5884–5904, https://doi.org/10.1016/j.gca.2009.05.067

Heumann, K., Gallus, S.M., Rädlinger, G. and Vogl, J. 1998. Precision and accuracy in isotope ratio measurements by plasma source mass spectrometry. *Journal of Analytical Atomic Spectrometry*, **13**, 1001, https://doi.org/10.1039/a801956g

Jaouen, K., Balter, V., Herrscher, E., Lamboux, A., Télouk, P. and Albarède, F. 2012. Fe and Cu stable isotopes in archeological human bones and their relationship to sex. *American Journal of Physical Anthropology*, **148**, 334–340, https://doi.org/10.1002/ajpa.22053

Jaouen, K., Gibert, M. *et al.* 2013a. Is aging recorded in blood Cu and Zn isotope compositions? *Metallomics*, **5**, 1016–1024, https://doi.org/10.1039/c3mt00085k

Jaouen, K., Pons, M.L. and Balter, V. 2013b. Iron, copper and zinc isotopic fractionation up mammal trophic chains. *Earth and Planetary Science Letters*, **374**, 164–172, https://doi.org/10.1016/j.epsl.2013.05.037

Jaouen, K., Beasley, M., Schoeninger, M., Hublin, J.J. and Richards, M.P. 2016a. Zinc isotope ratios of bones and teeth as new dietary indicators: results from a modern food web (Koobi Fora, Kenya). *Scientific Reports*, **6**, 26281, https://doi.org/10.1038/srep26281

Jaouen, K., Szpak, P. and Richards, M.P. 2016b. Zinc isotope ratios as indicators of diet and trophic level in arctic marine mammals. *PLoS ONE*, **11**, 1–13, https://doi.org/10.1371/journal.pone.0152299

Jaouen, K., Herrscher, E. and Balter, V. 2017. Copper and zinc isotope ratios in human bone and enamel. *American Journal of Physical Anthropology*, **162**, 491–500, https://doi.org/10.1002/ajpa.23132

Jaouen, K., Pouilloux, L., Balter, V., Pons, M.-L., Hublin, J.-J. and Albarède, F. 2019. Dynamic homeostasis modeling of Zn isotope ratios in the human body. *Metallomics*, **11**, 1049–1059, https://doi.org/10.1039/C8MT00286J

Jaouen, K., Trost, M., Bourgon, N., Colleter, R., Le Cabec, A. and Tütken, T. 2020. Zinc isotope variations in archeological human teeth (Lapa do Santo, Brazil) reveal dietary transitions in childhood and no contamination from gloves. *PLoS ONE*, **15**, e0232379, https://doi.org/10.1371/journal.pone.0232379

Jaouen, K., Villalba-Mouco, V. *et al.* 2022. A Neandertal dietary conundrum: insights provided by tooth enamel Zn isotopes from Gabasa, Spain. *Proceedings of the National Academy of Sciences*, **119**, e2109315119, https://doi.org/10.1073/pnas.2109315119

Jeong, H. 2022. Toxic metal concentrations and Cu–Zn–Pb isotopic compositions in tires. *Journal of Analytical Sciences and Technology*, **13**, 2, https://doi.org/10.1186/s40543-021-00312-3

Jeong, H. and Ra, K. 2021. Multi-isotope signatures (Cu, Zn, Pb) of different particle sizes in road-deposited sediments: a case study from industrial area. *Journal of Analytical Sciences and Technology*, **12**, 39, https://doi.org/10.1186/s40543-021-00292-4

Jeong, H., Ryu, J.S. and Ra, K. 2022. Characteristics of potentially toxic elements and multi-isotope signatures (Cu, Zn, Pb) in non-exhaust traffic emission sources. *Environmental Pollution*, **292**, 118339, https://doi.org/10.1016/j.envpol.2021.118339

Jeong, H., Araújo, D.F., Knoery, J., Briant, N. and Ra, K. 2023. Isotopic (Cu, Zn, and Pb) and elemental fingerprints of antifouling paints and their potential use for environmental forensic investigations. *Environmental Pollution*, **322**, 121176, https://doi.org/10.1016/j.envpol.2023.121176

John, S.G. and Conway, T.M. 2014. A role for scavenging in the marine biogeochemical cycling of zinc and zinc isotopes. *Earth and Planetary Science Letters*, **394**, 159–167, https://doi.org/10.1016/j.epsl.2014.02.053

John, S.G., Geis, R.W., Saito, M.A. and Boyle, E.A. 2007. Zinc isotope fractionation during high-affinity and low-affinity zinc transport by the marine diatom Thalassiosira oceanica. *Limnology and Oceanography*, **52**, 2710–2714, https://doi.org/10.4319/lo.2007.52.6.2710

John, S.G., Rouxel, O.J., Craddock, P.R., Engwall, A.M. and Boyle, E.A. 2008. Zinc stable isotopes in seafloor hydrothermal vent fluids and chimneys. *Earth and Planetary Science Letters*, **269**, 17–28, https://doi.org/10.1016/j.epsl.2007.12.011

Johnson, C.M., Beard, B.L. and Albarede, F. 2004. Overview and general concepts. *Reviews in Mineralogy and Geochemistry*, **55**, 1–24, https://doi.org/10.2138/gsrmg.55.1.1

Jouvin, D., Louvat, P., Juillot, F., Maréchal, C.N. and Benedetti, M.F. 2009. Zinc isotopic fractionation: why organic matters. *Environmental Science and Technology*, **43**, 5747–5754, https://doi.org/10.1021/es803012e

Jouvin, D., Weiss, D.J. *et al.* 2012. Stable isotopes of Cu and Zn in higher plants: evidence for Cu reduction at the root surface and two conceptual models for isotopic fractionation processes. *Environmental Science and Technology*, **46**, 2652–2660, https://doi.org/10.1021/es202587m

Juillot, F., Maréchal, C. *et al.* 2008. Zn isotopic fractionation caused by sorption on goethite and 2-Lines ferrihydrite. *Geochimica et Cosmochimica Acta*, **72**, 4886–4900, https://doi.org/10.1016/j.gca.2008.07.007

Junqueira, T.P., Araujo, D.F., Harrison, A.L., Sullivan, K. and Vriens, B. 2023. Contrasting copper concentrations and isotopic compositions in two Great Lakes watersheds. *Science of the Total Environment*, **904**, 166360, https://doi.org/10.1016/j.scitotenv.2023.166360

Kafantaris, F.C.A. and Borrok, D.M. 2014. Zinc isotope fractionation during surface adsorption and intracellular incorporation by bacteria. *Chemical Geology*, **366**, 42–51, https://doi.org/10.1016/j.chemgeo.2013.12.007

Kaur, K., Gupta, R., Saraf, S.A. and Saraf, S.K. 2014. Zinc: the metal of life. *Comprehensive Reviews in Food Science and Food Safety*, **13**, 358–376, https://doi.org/10.1111/1541-4337.12067

Kavner, A., John, S.G., Sass, S. and Boyle, E.A. 2008. Redox-driven stable isotope fractionation in transition metals: application to Zn electroplating. *Geochimica et Cosmochimica Acta*, **72**, 1731–1741, https://doi.org/10.1016/j.gca.2008.01.023

Kelley, K.D., Wilkinson, J.J., Chapman, J.B., Crowther, H.L. and Weiss, D.J. 2009. Zinc isotopes in sphalerite from base metal deposits in the Red Dog district, northern Alaska. *Economic Geology*, **104**, 767–773, https://doi.org/10.2113/gsecongeo.104.6.767

Kent, D.B., Abrams, R.H., Davis, J.A., Coston, J.A. and LeBlanc, D.R. 2000. Modeling the influence of variable pH on the transport of zinc in a contaminated aquifer using semiempirical surface complexation models. *Water Resources Research*, **36**, 3411–3425, https://doi.org/10.1029/2000WR900244

Köbberich, M. and Vance, D. 2019. Zn isotope fractionation during uptake into marine phytoplankton: implications for oceanic zinc isotopes. *Chemical Geology*, **523**, 154–161, https://doi.org/10.1016/j.chemgeo.2019.04.004

Krayenbuehl, P.-A., Walczyk, T., Schoenberg, R., von Blanckenburg, F. and Schulthess, G. 2005. Hereditary hemochromatosis is reflected in the iron isotope composition of blood. *Blood*, **105**, 3812–3816, https://doi.org/10.1182/blood-2004-07-2807

Kyser, T.K., Leybourne, M.I. and Layton-Matthews, D. 2020. Advances in the use of isotopes in geochemical exploration: instrumentation and applications in understanding geochemical processes. *Geochemistry: Exploration, Environment, Analysis*, **20**, 199–204, https://doi.org/10.1144/geochem2019-045

Larner, F., Woodley, L.N. *et al.* 2015. Zinc isotopic compositions of breast cancer tissue. *Metallomics*, **7**, 112–117, https://doi.org/10.1039/c4mt00260a

Leybourne, M.I., Goodfellow, W.D., Boyle, D.R. and Hall, G.E.M. 2000. Form and distribution of gold mobilized into surface waters and sediments from a Gossan tailings pile, Murray Brook massive sulphide deposit, New Brunswick, Canada. *Applied Geochemistry*, **15**, 629–646, https://doi.org/10.1016/S0883-2927(99)00068-2

Li, W., Gou, W., Li, W., Zhang, T., Yu, B., Liu, Q. and Shi, J. 2019. Environmental applications of metal stable isotopes: silver, mercury and zinc. *Environmental Pollution*, **252**, 1344–1356, https://doi.org/10.1016/j.envpol.2019.06.037

Liang, B., Han, G., Zeng, J., Qu, R., Liu, M., Liu, J. and Zhao, Y. 2022. Zn isotope fractionation in laterites from Yunnan province, southwest China: implications for the Zn cycles and its environmental impacts in (sub-) tropics. *Science of the Total Environment*, **844**, 157245, https://doi.org/10.1016/j.scitotenv.2022.157245

Little, S.H., Vance, D., Walker-Brown, C. and Landing, W.M. 2014. The oceanic mass balance of copper and zinc isotopes, investigated by analysis of their inputs, and outputs to ferromanganese oxide sediments. *Geochimica et Cosmochimica Acta*, **125**, 673–693, https://doi.org/10.1016/j.gca.2013.07.046

Liu, S.A., Wang, Z.Z., Li, S.G., Huang, J. and Yang, W. 2016. Zinc isotope evidence for a large-scale carbonated mantle beneath eastern China. *Earth and Planetary Science Letters*, **444**, 169–178, https://doi.org/10.1016/j.epsl.2016.03.051

Liu, Y., Gao, T. *et al.* 2020. Using Zn isotopes to trace Zn sources and migration pathways in paddy soils around mining area. *Environmental Pollution*, **267**, 115616, https://doi.org/10.1016/j.envpol.2020.115616

Liu, X., Huang, Y. *et al.* 2023. Soil (microbial) disturbance affect the zinc isotope biogeochemistry but has little effect on plant zinc uptake. *Science of The Total Environment*, **875**, 162490, https://doi.org/10.1016/j.scitotenv.2023.162490

Luck, J.M., Othman, D.B. and Albarède, F. 2005. Zn and Cu isotopic variations in chondrites and iron meteorites: early solar nebula reservoirs and parent-body processes. *Geochimica et Cosmochimica Acta*, **69**, 5351–5363, https://doi.org/10.1016/j.gca.2005.06.018

Lum, K.R., Kaiser, K.L.E. and Jaskot, C. 1991. Distribution and fluxes of metals in the St. Lawrence River from the outflow of Lake Ontario to Quebec City. *Aquatic Sciences*, **53**, 1–19, https://doi.org/10.1007/BF00877072

Ma, L., Wang, W., Xie, M.W., Wang, W.X. and Evans, R.D. 2020. Using Zn isotopic signatures for source identification in a contaminated estuary of Southern China. *Environmental Science & Technology*, **54**, 5140–5149, https://doi.org/10.1021/acs.est.9b05955

Mahan, B., Moynier, F., Lund Jørgensen, A., Habekost, M. and Siebert, J. 2018. Examining the homeostatic distribution of metals and Zn isotopes in Göttingen minipigs. *Metallomics*, **10**, 1264–1281, https://doi.org/10.1039/C8MT00179K

Mahan, B., Chung, R.S., Pountney, D.L., Moynier, F. and Turner, S. 2020. Isotope metallomics approaches for medical research. *Cellular and Molecular Life Sciences*, **77**, 3293–3309, https://doi.org/10.1007/s00018-020-03484-0

Mahowald, N.M., Yoshioka, M., Collins, W.D., Conley, A.J., Fillmore, D.W. and Coleman, D.B. 2006. Climate response and radiative forcing from mineral aerosols during the last glacial maximum, pre-industrial, current and doubled-carbon dioxide climates. *Geophysical Research Letters*, **33**, https://doi.org/10.1029/2006GL026126

Maréchal, C.N., Télouk, P. and Albarède, F. 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, **156**, 251–273, https://doi.org/10.1016/S0009-2541(98)00191-0

Maréchal, C.N., Nicolas, E., Douchet, C. and Albarède, F. 2000. Abundance of zinc isotopes as a marine biogeochemical tracer. *Geochemistry, Geophysics, Geosystems*, **1**, https://doi.org/10.1029/1999GC000029

Maret, W. 2013. Zinc biochemistry: from a single zinc enzyme to a key element of life. *Advances in Nutrition*, **4**, 82–91, https://doi.org/10.3945/an.112.003038

Martín, A., Caldelas, C., Weiss, D., Aranjuelo, I. and Navarro, E. 2018. Assessment of metal immission in urban environments using elemental concentrations and Zinc isotope signatures in leaves of *Nerium oleander*. *Environmental Science & Technology*, **52**, 2071–2080, https://doi.org/10.1021/acs.est.7b00617

Mason, R.P. 2013. *Trace Metals in Aquatic Systems*. Wiley, https://doi.org/10.1002/9781118274576

Mason, T.F., Weiss, D.J. *et al.* 2005. Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia. *Chemical Geology*, **221**, 170–187, https://doi.org/10.1016/j.chemgeo.2005.04.011

Mathur, R. and Wang, D. 2019. Transition metal isotopes applied to exploration geochemistry. *In*: Decrée, S. and Robb, L. (eds) *Ore Deposits*, 163–183, American Geophysical Union, https://doi.org/10.1002/9781119290544.ch7

Mathur, R., Mahan, B. *et al.* 2021. Fingerprinting the Cretaceous–Paleogene boundary impact with Zn isotopes. *Nature Communications*, **12**, 4128, https://doi.org/10.1038/s41467-021-24419-8

Mattielli, N., Petit, J.C. *et al.* 2009. Zn isotope study of atmospheric emissions and dry depositions within a 5 km radius of a Pb–Zn refinery. *Atmospheric Environment*, **43**, 1265–1272, https://doi.org/10.1016/j.atmosenv.2008.11.030

Mavromatis, V., González, A.G., Dietzel, M., and Schott, J. 2019. Zinc isotope fractionation during the inorganic precipitation of calcite – towards a new pH proxy. *Geochimica et Cosmochimica Acta*, **244**, 99–112, https://doi.org/10.1016/j.gca.2018.09.005

McCormack, J., Szpak, P. *et al.* 2021. Zinc isotopes from archaeological bones provide reliable trophic level information for marine mammals. *Communications Biology*, **4**, 683, https://doi.org/10.1038/s42003-021-02212-z

McCormack, J., Griffiths, M.L. *et al.* 2022. Trophic position of Otodus megalodon and great white sharks through time revealed by zinc isotopes. *Nature Communications*, **13**, 2980, https://doi.org/10.1038/s41467-022-30528-9

Meylan, G. and Reck, B.K. 2017. The anthropogenic cycle of zinc: status quo and perspectives. *Resources, Conservation and Recycling*, **123**, 1–10, https://doi.org/10.1016/j.resconrec.2016.01.006

Moeller, K., Schoenberg, R., Pedersen, R.-B., Weiss, D. and Dong, S. 2012. Calibration of the new certified reference materials ERM-AE633 and ERM-AE647 for copper and IRMM-3702 for zinc isotope amount ratio determinations. *Geostandards and Geoanalytical Research*, **36**, 177–199, https://doi.org/10.1111/j.1751-908X.2011.00153.x

Mondillo, N., Wilkinson, J.J., Boni, M., Weiss, D.J. and Mathur, R. 2018. A global assessment of Zn isotope fractionation in secondary Zn minerals from sulfide and non-sulfide ore deposits and model for fractionation control. *Chemical Geology*, **500**, 182–193, https://doi.org/10.1016/j.chemgeo.2018.09.033

Moore, R.E., Rehkämper, M., Maret, W. and Larner, F. 2019. Assessment of coupled Zn concentration and natural stable isotope analyses of urine as a novel probe of Zn status. *Metallomics*, **11**, 1506–1517, https://doi.org/10.1039/C9MT00160C

Moynier, F., Beck, P., Jourdan, F., Yin, Q.Z., Reimold, U. and Koeberl, C. 2009*a*. Isotopic fractionation of zinc in tektites. *Earth and Planetary Science Letters*, **277**, 482–489, https://doi.org/10.1016/j.epsl.2008.11.020

Moynier, F., Pichat, S., Pons, M.L., Fike, D., Balter, V. and Albarède, F. 2009*b*. Isotopic fractionation and transport mechanisms of Zn in plants. *Chemical Geology*, **267**, 125–130, https://doi.org/10.1016/j.chemgeo.2008.09.017

Moynier, F., Beck, P. *et al.* 2010. Volatilization induced by impacts recorded in Zn isotope composition of ureilites. *Chemical Geology*, **276**, 374–379, https://doi.org/10.1016/j.chemgeo.2010.07.005

Moynier, F., Fujii, T., Shaw, A.S. and Le Borgne, M. 2013. Heterogeneous distribution of natural zinc isotopes in mice. *Metallomics*, **5**, 693, https://doi.org/10.1039/c3mt00008g

Moynier, F., Vance, D., Fujii, T. and Savage, P. 2017. The isotope geochemistry of zinc and copper. *Reviews in Mineralogy and Geochemistry*, **82**, 543–600, https://doi.org/10.2138/rmg.2017.82.13

Moynier, F., Borgne, M.L., Lahoud, E., Mahan, B., Mouton-Liger, F., Hugon, J. and Paquet, C. 2020. Copper and zinc isotopic excursions in the human brain affected by Alzheimer's disease. *Alzheimer's & Dementia: Diagnosis, Assessment & Disease Monitoring*, **12**, e12112, https://doi.org/10.1002/dad2.12112

Müsing, K., Clarkson, M.O. and Vance, D. 2022. The meaning of carbonate Zn isotope records: constraints from a detailed geochemical and isotope study of bulk deep-sea carbonates. *Geochimica et Cosmochimica Acta*, **324**, 26–43, https://doi.org/10.1016/j.gca.2022.02.029

Norbu, N., Wang, S., Xu, Y., Yang, J. and Liu, Q. 2017. Application of zinc isotope tracer technology in tracing soil heavy metal pollution. *In*: *AIP Conference Proceedings*, **1864**, 020223. AIP Publishing, https://doi.org/10.1063/1.4993040

Ochieng, E.Z., Lalah, J.O. and Wandiga, S.O. 2008. Water quality and trace metal distribution in a Pristine Lake in the Lake Basin in Kenya. *Bulletin of Environmental Contamination and Toxicology*, **80**, 362–368, https://doi.org/10.1007/s00128-008-9372-2

Ochoa Gonzalez, R. and Weiss, D. 2015. Zinc isotope variability in three coal-fired power plants: a predictive model for determining isotopic fractionation during combustion. *Environmental Science & Technology*, **49**, 12560–12567, https://doi.org/10.1021/acs.est.5b02402

Paniello, R.C., Moynier, F., Beck, P., Barrat, J.A., Podosek, F.A. and Pichat, S. 2012. Zinc isotopes in HEDs: clues to the formation of 4-Vesta, and the unique composition of Pecora Escarpment 82502. *Geochimica et Cosmochimica Acta*, **86**, 76–87, https://doi.org/10.1016/j.gca.2012.01.045

Pašava, J., Tornos, F. and Chrastný, V. 2014. Zinc and sulfur isotope variation in sphalerite from carbonate-hosted zinc deposits, Cantabria, Spain. *Mineralium Deposita*, **49**, 797–807, https://doi.org/10.1007/s00126-014-0535-2

Peel, K., Weiss, D., Chapman, J., Arnold, T. and Coles, B. 2008. A simple combined sample–standard bracketing and inter-element correction procedure for accurate mass bias correction and precise Zn and Cu isotope ratio measurements. *Journal of Analytical Atomic Spectrometry*, **23**, 103, https://doi.org/10.1039/b710977f

Peel, K., Weiss, D. and Siggc, L. 2009. Zinc isotope composition of settling particles as a proxy for biogeochemical processes in lakes: insights from the eutrophic Lake Greifen, Switzerland. *Limnology and Oceanography*, **54**, 1699–1708, https://doi.org/10.4319/lo.2009.54.5.1699

Petit, J.C., Schäfer, J. *et al.* 2015. The estuarine geochemical reactivity of Zn isotopes and its relevance for the biomonitoring of anthropogenic Zn and Cd contaminations from metallurgical activities: example of the Gironde fluvial-estuarine system, France. *Geochimica et Cosmochimica Acta*, **170**, 108–125, https://doi.org/10.1016/j.gca.2015.08.004

Pichat, S., Douchet, C. and Albarède, F. 2003. Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka. *Earth and Planetary Science Letters*, **210**, 167–178, https://doi.org/10.1016/S0012-821X(03)00106-7

Pokrovsky, O.S., Viers, J. and Freydier, R. 2005. Zinc stable isotope fractionation during its adsorption on oxides and hydroxides. *Journal of Colloid and Interface Science*, **291**, 192–200, https://doi.org/10.1016/j.jcis.2005.04.079

Rehkämper, M., Wombacher, F., Horner, T.J. and Xue, Z. 2012. Natural and anthropogenic Cd isotope variations. *In*: Baskaran, M. (ed.) *Handbook of Environmental Isotope Geochemistry*, **I**, 125–154, Springer, https://doi.org/10.1007/978-3-642-10637-8_8

Resano, M., Aramendía, M., Rello, L., Calvo, M.L., Bérail, S. and Pécheyran, C. 2013. Direct determination of Cu isotope ratios in dried urine spots by means of fs-LA-MC-ICPMS. Potential to diagnose Wilson's disease. *Journal of Analytical Atomic Spectrometry*, **28**, 98–106, https://doi.org/10.1039/C2JA30262D

Rink, L. 2000. Zinc and the immune system. *Proceedings of the Nutrition Society*, **59**, 541–552, https://doi.org/10.1017/S0029665100000781

Rink, L. and Haase, H. 2007. Zinc homeostasis and immunity. *Trends in Immunology*, **28**, 1–4, https://doi.org/10.1016/j.it.2006.11.005

Sauzéat, L., Bernard, E. *et al.* 2018. Isotopic evidence for disrupted copper metabolism in amyotrophic lateral sclerosis. *iScience*, **6**, 264–271, https://doi.org/10.1016/j.isci.2018.07.023

Schilling, K., Larner, F. *et al.* 2020. Urine metallomics signature as an indicator of pancreatic cancer. *Metallomics*, **12**, 752–757, https://doi.org/10.1039/D0MT00061B

Schilling, K., Moore, R.E.T. *et al.* 2021. Zinc stable isotopes in urine as diagnostic for cancer of secretory organs. *Metallomics*, **13**, mfab020, https://doi.org/10.1093/mtomcs/mfab020

Schilling, K., Harris, A.L., Halliday, A.N., Schofield, C.J., Sheldon, H., Haider, S. and Larner, F. 2022. Investigations on zinc isotope fractionation in breast cancer tissue using in vitro cell culture uptake-efflux experiments. *Frontiers in Medicine*, **8**, https://doi.org/10.3389/fmed.2021.746532

Schleicher, N.J., Dong, S. *et al.* 2020. A global assessment of copper, zinc, and lead isotopes in mineral dust sources and aerosols. *Frontiers Earth Sciences*, **8**, https://doi.org/10.3389/feart.2020.00167

Schoenberg, R. and von Blanckenburg, F. 2005. An assessment of the accuracy of stable Fe isotope ratio measurements on samples with organic and inorganic matrices by high-resolution multicollector ICP-MS. *International Journal of Mass Spectrometry*, **242**, 257–272, https://doi.org/10.1016/j.ijms.2004.11.025

Schöne, B.R. and Krause, R.A., Jr 2016. Retrospective environmental biomonitoring – Mussel Watch expanded. *Global and Planetary Change*, **144**, 228–251, https://doi.org/10.1016/j.gloplacha.2016.08.002

Shiel, A.E., Weis, D. and Orians, K.J. 2012. Tracing cadmium, zinc and lead sources in bivalves from the coasts of western Canada and the USA using isotopes. *Geochimica et Cosmochimica Acta*, **76**, 175–190, https://doi.org/10.1016/j.gca.2011.10.005

Shiel, A.E., Weis, D., Cossa, D. and Orians, K.J. 2013. Determining provenance of marine metal pollution in French bivalves using Cd, Zn and Pb isotopes. *Geochimica et Cosmochimica Acta*, **121**, 155–167, https://doi.org/10.1016/j.gca.2013.07.005

Shiller, A.M. and Boyle, E. 1985. Dissolved zinc in rivers. *Nature*, **317**, 49–52, https://doi.org/10.1038/317049a0

Sivry, Y., Riotte, J. *et al.* 2008. Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters The Riou Mort–Lot River system. *Chemical Geology*, **255**, 295–304, https://doi.org/10.1016/j.chemgeo.2008.06.038

Skierszkan, E.K., Mayer, K.U., Weis, D. and Beckie, R.D. 2016. Molybdenum and zinc stable isotope variation in mining waste rock drainage and waste rock at the Antamina mine, Peru. *Science of the Total Environment*, **550**, 103–113, https://doi.org/10.1016/j.scitotenv.2016.01.053

Sonke, J.E., Sivry, Y. *et al.* 2008. Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter. *Chemical Geology*, **252**, 145–157, https://doi.org/10.1016/j.chemgeo.2008.02.006

Sossi, P.A., Halverson, G.P., Nebel, O. and Eggins, S.M. 2015. Combined separation of Cu, Fe and Zn from rock matrices and improved analytical protocols for stable isotope determination. *Geostandards and Geoanalytical Research*, **39**, 129–149, https://doi.org/10.1111/j.1751-908X.2014.00298.x

Souto-Oliveira, C.E., Babinski, M., Araújo, D.F. and Andrade, M.F. 2018. Multi-isotopic fingerprints (Pb, Zn, Cu) applied for urban aerosol source apportionment and discrimination. *Science of the Total Environment*, **626**, 1350–1366, https://doi.org/10.1016/j.scitotenv.2018.01.192

Souto-Oliveira, C.E., Babinski, M., Araújo, D.F., Weiss, D.J. and Ruiz, I.R. 2019. Multi-isotope approach of Pb, Cu and Zn in urban aerosols and anthropogenic sources improves tracing of the atmospheric pollutant sources in megacities. *Atmospheric Environment*, **198**, 427–437, https://doi.org/10.1016/j.atmosenv.2018.11.007

Sparks, D.L. 2005. Toxic metals in the environment: the role of surfaces. *Elements*, **1**, 193–197, https://doi.org/10.2113/gselements.1.4.193

Sullivan, K., Moore, R.E.T., Rehkämper, M., Layton-Matthews, D., Leybourne, M.I., Puxty, J. and Kyser, T.K. 2020. Postprandial zinc stable isotope response in human blood serum. *Metallomics*, **9**, 1380–1388, https://doi.org/10.1039/D0MT00122H

Sullivan, K.V., Moore, R.E.T. *et al.* 2021. Zinc stable isotope analysis reveals Zn dyshomeostasis in benign tumours, breast cancer, and adjacent histologically normal tissue. *Metallomics*, **13**, mfab027, https://doi.org/10.1093/mtomcs/mfab027

Sullivan, K.V., Moore, R.E.T. and Vanhaecke, F. 2023. The influence of physiological and lifestyle factors on essential mineral element isotopic compositions in the human body: implications for the design of isotope metallomics research. *Metallomics*, **15**, mfad012, https://doi.org/10.1093/mtomcs/mfad012

Szynkiewicz, A. and Borrok, D.M. 2016. Isotope variations of dissolved Zn in the Rio Grande watershed, USA: the role of adsorption on Zn isotope composition. *Earth and Planetary Science Letters*, **433**, 293–302, https://doi.org/10.1016/j.epsl.2015.10.050

Takano, S., Tanimizu, M., Hirata, T., Shin, K.C., Fukami, Y., Suzuki, K. and Sohrin, Y. 2017. A simple and rapid method for isotopic analysis of nickel, copper, and zinc in seawater using chelating extraction and anion exchange. *Analytica Chimica Acta*, **967**, 1–11, https://doi.org/10.1016/j.aca.2017.03.010

Tapiero, H. and Tew, K.D. 2003. Trace elements in human physiology and pathology: zinc and metallothioneins. *Biomedicine & Pharmacotherapy*, **57**, 399–411, https://doi.org/10.1016/S0753-3322(03)00081-7

Telus, M., Dauphas, N. *et al.* 2012. Iron, zinc, magnesium and uranium isotopic fractionation during continental crust differentiation: the tale from migmatites, granitoids, and pegmatites. *Geochimica et Cosmochimica Acta*, **97**, 247–265, https://doi.org/10.1016/j.gca.2012.08.024

Thapalia, A., Borrok, D.M., Van Metre, P.C. and Wilson, J. 2015. Zinc isotopic signatures in eight lake sediment cores from across the United States. *Environmental Science & Technology*, **49**, 132–140, https://doi.org/10.1021/es5036893

Tonhá, M.S., Garnier, J. *et al.* 2020. Behavior of metallurgical zinc contamination in coastal environments: a survey of Zn from electroplating wastes and partitioning in sediments. *Science of the Total Environment*, **743**, 140610, https://doi.org/10.1016/j.scitotenv.2020.140610

Toutain, J.P., Sonke, J., Munoz, M., Nonell, A., Polvé, M., Viers, J. and Sumarti, S. 2008. Evidence for Zn isotopic fractionation at Merapi volcano. *Chemical Geology*, **253**, 74–82, https://doi.org/10.1016/j.chemgeo.2008.04.007

Truong-Tran, A.Q., Carter, J., Ruffin, R. and Zalewski, P.D. 2001. New insights into the role of zinc in the respiratory epithelium. *Immunology & Cell Biology*, **79**, 170–177, https://doi.org/10.1046/j.1440-1711.2001.00986.x

Turner, A. and Millward, G.E. 2000. Particle dynamics and trace metal reactivity in estuarine plumes. *Estuarine, Coastal and Shelf Science*, **50**, 761–774, https://doi.org/10.1006/ecss.2000.0589

Vance, D., Matthews, A., Keech, A., Archer, C., Hudson, G., Pett-Ridge, J. and Chadwick, O.A. 2016. The behaviour of Cu and Zn isotopes during soil development: controls on the dissolved load of rivers. *Chemical Geology*, **445**, 36–53, https://doi.org/10.1016/j.chemgeo.2016.06.002

Vanhaecke, F. and Costas-Rodríguez, M. 2021. High-precision isotopic analysis of essential mineral elements: capabilities as a diagnostic/prognostic tool. *View*, **2**, 20200094, https://doi.org/10.1002/VIW.20200094

Van Heghe, L. 2013. *The Development and Evaluation of Analytical Methods Based on Multi-Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) for High-Precision Isotopic Analysis of Cu, Fe and Zn in Human Blood, Applicable in Medical Diagnosis*. PhD thesis, Ghent University, https://biblio.ugent.be/publication/4212647 [last accessed 19 March 2024].

Van Heghe, L., Engström, E., Rodushkin, I., Cloquet, C. and Vanhaecke, F. 2012. Isotopic analysis of the metabolically relevant transition metals Cu, Fe and Zn in human blood from vegetarians and omnivores using multi-collector ICP-mass spectrometry. *Journal of Analytical Atomic Spectrometry*, **27**, 1327–1334, https://doi.org/10.1039/c2ja30070b

Van Heghe, L., Delanghe, J., Van Vlierberghe, H. and Vanhaecke, F. 2013. The relationship between the iron isotopic composition of human whole blood and iron status parameters. *Metallomics*, **5**, 1503–1509.

Van Heghe, L., Deltombe, O., Delanghe, J., Depypere, H. and Vanhaecke, F. 2014. The influence of menstrual blood loss and age on the isotopic composition of Cu, Fe and Zn in human whole blood. *Journal of Analytical Atomic Spectrometry*, **29**, 478–482, https://doi.org/10.1039/C3JA50269D

Vašák, M. and Hasler, D.W. 2000. Metallothioneins: new functional and structural insights. *Current Opinion in Chemical Biology*, **4**, 177–183, https://doi.org/10.1016/S1367-5931(00)00082-X

Veeramani, H., Eagling, J., Jamieson-Hanes, J.H., Kong, L., Ptacek, C.J. and Blowes, D.W. 2015. Zinc isotope fractionation as an indicator of geochemical attenuation processes. *Environmental Science & Technology Letters*, **2**, 314–319, https://doi.org/10.1021/acs.estlett.5b00273

Viers, J., Oliva, P. *et al.* 2007. Evidence of Zn isotopic fractionation in a soil-plant system of a pristine tropical watershed (Nsimi, Cameroon). *Chemical Geology*, **239**, 124–137, https://doi.org/10.1016/j.chemgeo.2007.01.005

Viers, J., Prokushkin, A.S. *et al.* 2015. Zn isotope fractionation in a pristine larch forest on permafrost-dominated soils in Central Siberia. *Geochemical Transactions*, **16**, 1–15, https://doi.org/10.1186/s12932-015-0018-0

Wang, L., Jin, Y. *et al.* 2021. Possible application of stable isotope compositions for the identification of metal sources in soil. *Journal of Hazardous Materials*, **407**, 124812, https://doi.org/10.1016/j.jhazmat.2020.124812

Wanty, R.B., Podda, F., De Giudici, G., Cidu, R. and Lattanzi, P. 2013. Zinc isotope and transition-element dynamics accompanying hydrozincite biomineralization in the Rio Naracauli, Sardinia, Italy. *Chemical Geology*, **337–338**, 1–10, https://doi.org/10.1016/j.chemgeo.2012.11.010

Wanty, R.B., Balistrieri, L.S. *et al.* 2017. *In vivo* isotopic fractionation of zinc and biodynamic modeling yield insights into detoxification mechanisms in the mayfly *Neocloeon triangulifer*. *Science of The Total Environment*, **609**, 1219–1229, https://doi.org/10.1016/j.scitotenv.2017.07.269

Weber, T., John, S., Tagliabue, A. and DeVries, T. 2018. Biological uptake and reversible scavenging of zinc in the global ocean. *Science*, **361**, 72–76, https://doi.org/10.1126/science.aap8532

Weinstein, C., Moynier, F., Wang, K., Paniello, R., Foriel, J., Catalano, J. and Pichat, S. 2011. Isotopic fractionation of Cu in plants. *Chemical Geology*, **286**, 266–271, https://doi.org/10.1016/j.chemgeo.2011.05.010

Weiss, D.J., Mason, T.F., Zhao, F.J., Kirk, G.J.D., Coles, B.J. and Horstwood, M.S.A. 2005. Isotopic discrimination of zinc in higher plants. *New Phytologist*, **165**, 703–710, https://doi.org/10.1111/j.1469-8137.2004.01307.x

Weiss, D.J., Rausch, N. *et al.* 2007. Atmospheric deposition and isotope biogeochemistry of zinc in ombrotrophic peat. *Geochimica et Cosmochimica Acta*, **71**, 3498–3517, https://doi.org/10.1016/j.gca.2007.04.026

Weiss, D., Northover, G., Hanif, M., García-España, E., Vilar, R., Arnold, T. and Delgado, E. 2021. Isotope fractionation of zinc in the paddy rice soil–water environment and the role of 2′deoxymugineic acid (DMA) as zincophore under Zn limiting conditions. *Chemical Geology*, **577**, 120271, https://doi.org/10.1016/j.chemgeo.2021.120271

Wiederhold, J.G. 2015. Metal stable isotope signatures as tracers in environmental geochemistry. *Environmental Science & Technology*, **49**, 2606–2624, https://doi.org/10.1021/es504683e

Wiggenhauser, M., Bigalke, M., Imseng, M., Keller, A., Archer, C., Wilcke, W. and Frossard, E. 2018. Zinc isotope fractionation during grain filling of wheat and a comparison of zinc and cadmium isotope ratios in identical soil–plant systems. *New Phytologist*, **219**, 195–205, https://doi.org/10.1111/nph.15146

Wilkinson, J.J. 2023. The potential of Zn isotopes in the science and exploration of ore deposits. *In*: Huston, D. and Gutzmer, J. (eds) *Isotopes in Economic Geology, Metallogenesis and Exploration*. Springer International, Cham, 451–463, https://doi.org/10.1007/978-3-031-27897-6_15

Wilkinson, J.J., Weiss, D.J., Mason, T.F.D. and Coles, B.J. 2005. Zinc isotope variation in hydrothermal systems: preliminary evidence from the Irish

Midlands ore field. *Economic Geology*, **100**, 583–590, https://doi.org/10.2113/gsecongeo.100.3.583

Wisawapipat, W., Janlaksana, Y. and Christl, I. 2017. Zinc solubility in tropical paddy soils: a multi-chemical extraction technique study. *Geoderma*, **301**, 1–10, https://doi.org/10.1016/j.geoderma.2017.04.002

Wong, C.S.C., Li, X. and Thornton, I. 2006. Urban environmental geochemistry of trace metals. *Environmental Pollution*, **142**, 1–16, https://doi.org/10.1016/j.envpol.2005.09.004

Xia, Y., Gao, T. *et al.* 2020. Zinc isotope revealing zinc's sources and transport processes in karst region. *Science of the Total Environment*, **724**, 138191, https://doi.org/10.1016/j.scitotenv.2020.138191

Xie, Y., Zhang, Q., Wang, L., Wang, Y., Cheng, Z., Yang, Z. and Yang, W. 2019. The effects of partially or completely substituted dietary zinc sulfate by lower levels of zinc methionine on growth performance, apparent total tract digestibility, immune function, and visceral indices in weaned piglets. *Animals*, **9**, 236, https://doi.org/10.3390/ani9050236

Yang, Y., Zhang, X. *et al.* 2018. Calibrating NIST SRM 683 as a new international reference standard for Zn isotopes. *Journal of Analytical Atomic Spectrometry*, **33**, 1777–1783, https://doi.org/10.1039/C8JA00249E

Yin, N.H., Sivry, Y., Benedetti, M.F., Lens, P.N.L. and van Hullebusch, E.D. 2015. Application of Zn isotopes in environmental impact assessment of Zn–Pb metallurgical industries: a mini review. *Applied Geochemistry*, **64**, 128–135, https://doi.org/10.1016/j.apgeochem.2015.09.016

Yin, N.H., Sivry, Y., Benedetti, M.F., Lens, P.N. and van Hullebusch, E.D. 2016. Application of Zn isotopes in environmental impact assessment of Zn–Pb metallurgical industries: a mini review. *Applied Geochemistry*, **64**, 128–135, https://doi.org/10.1016/j.apgeochem.2015.09.016

Yin, N.H., Van Hullebusch, E.D., Benedetti, M., Lens, P.N. and Sivry, Y. 2018. Zn isotopes fractionation during slags' weathering: one source of contamination, multiple isotopic signatures. *Chemosphere*, **195**, 483–490, https://doi.org/10.1016/j.chemosphere.2017.11.184

Zhang, X.Y., Chen, L.H. *et al.* 2022*a*. Zinc isotopic evidence for recycled carbonate in the deep mantle. *Nature Communications*, **13**, 6085, https://doi.org/10.1038/s41467-022-33789-6

Zhang, X., Huang, J., Gong, Y., Zhang, L. and Huang, F. 2022*b*. Climate influence on zinc isotope variations in a loess–paleosol sequence of the Chinese Loess Plateau. *Geochimica et Cosmochimica Acta*, **321**, 115–132, https://doi.org/10.1016/j.gca.2022.01.023

Zhao, Y., Vance, D., Abouchami, W. and De Baar, H.J. 2014. Biogeochemical cycling of zinc and its isotopes in the Southern Ocean. *Geochimica et Cosmochimica Acta*, **125**, 653–672, https://doi.org/10.1016/j.gca.2013.07.045

Zhou, Q., Zhang, J., Fu, J., Shi, J. and Jiang, G. 2008. Biomonitoring: an appealing tool for assessment of metal pollution in the aquatic ecosystem. *Analytica Chimica Acta*, **606**, 135–150, https://doi.org/10.1016/j.aca.2007.11.018

Zhu, Z.Y., Jiang, S.Y., Yang, T. and Wei, H.Z. 2015. Improvements in Cu–Zn isotope analysis with MC-ICP-MS: a revisit of chemical purification, mass spectrometry measurement and mechanism of Cu/Zn mass bias decoupling effect. *International Journal of Mass Spectrometry*, **393**, 34–40, https://doi.org/10.1016/j.ijms.2015.10.009

Zimmermann, T., Mohamed, A.F., Reese, A., Wieser, M.E., Kleeberg, U., Pröfrock, D. and Irrgeher, J. 2020. Zinc isotopic variation of water and surface sediments from the German Elbe River. *Science of the Total Environment*, **707**, 135219, https://doi.org/10.1016/j.scitotenv.2019.135219